TRACE ELEMENTS IN NEW ZEALAND OILS

THEIR SIGNIFICANCE FOR ANALYTICAL CHEMISTRY, GEOCHEMISTRY AND OIL CLASSIFICATION

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ABSTRACT

This work is a study of trace elements in New Zealand and some overseas oils. Trace elements have been successfully used in previous studies to distinguish marine oils of different origins, to identify groups of related oils in individual regional areas and to establish migration patterns.

This is the first study of trace element concentrations and variations in New Zealand crude oils. A wide range of oil samples of different origins and geographical regions was analysed and the obtained trace element concentrations enabled a comprehensive comparison of trace element contents in terrestrial, lacustrine and marine oils. Over 120 oil samples of various marine and terrestrial origins were analysed for 42 elements and the resulting trace element concentrations were subjected to correlation and principal components analysis.

The trace element concentrations in New Zealand oils are very similar to those in other terrestrial-derived crude oils. Elements, associated with clay minerals had a high mutual correlation and were present in concentrations, comparable with, or exceeding those in marine oils. The origin of these elements and their implications to the classification of Taranaki Basin oils are discussed.

Trace elements in the asphaltene fractions of some New Zealand and overseas oils, in extracts of coal from the Pakawau Group and in ashed coal samples were determined to obtain additional information about the origin of Taranaki Basin oils.

In this study, 42 trace elements were determined by instrumental neutron activation analysis, graphite furnace atomic absorption and inductively coupled plasma emission spectrometry. Instrumental NAA was used to quantify a wide range of elements in undiluted and untreated crude oils. Graphite furnace AAS is a more sensitive method for some elements and was used to determine trace elements that were not detectable by INAA.

The analysis of organic oil solutions was difficult due to the complex organic oil matrix. Various ashing, low temperature ashing, acid oxidation and extraction techniques were investigated and were considered to be unsuitable for the quantification of low amounts of elements in crude oils. A mixed-solvent system, using toluene and isopropanol, enabled the use of ready available aqueous standards and allowed the quantification of trace elements other than those present in the standard oil solutions. The close matching of standard and sample solutions was essential for the accuracy of the trace element results. Various analytical techniques, their use and suitability for the analysis of crude oils are discussed in detail.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

APPENDICES

I. INTRODUCTION

This thesis is a study of trace elements and their interelemental correlations in New Zealand and overseas oils. Trace elements, mainly nickel and vanadium, have been used in classification schemes for marine oils, but few studies have investigated the trace element content of terrestrial-derived oils or compared a wide range of samples. Oils of terrestrial, lacustrine and marine origin from various countries were studied and Ni and V, as well as a wide range of other trace elements were determined and statistically evaluated.

Analytical methods used included instrumental neutron activation analysis, graphite furnace atomic absorption and inductively coupled plasma emission spectrometry. The use of different analytical techniques made possible the determination of a wide range of elements.

This thesis is the first study of trace elements in New Zealand oils and confirmed their terrestrial origin. The determined trace element concentrations and variations allowed for discrimination of oils according to their different origins.

1.1 PREVIOUS WORK

Crude oils are usually classified and characterized according to their hydrocarbon composition, and biomarkers[1] are frequently used for oil-oil and oil-source rock classifications (*Tissot* and *Welte 1984)*. The presence of trace metals, mainly Ni, V and Fe, in crude oils and their significance in providing information about the geological history of the oils has been known for a long time.

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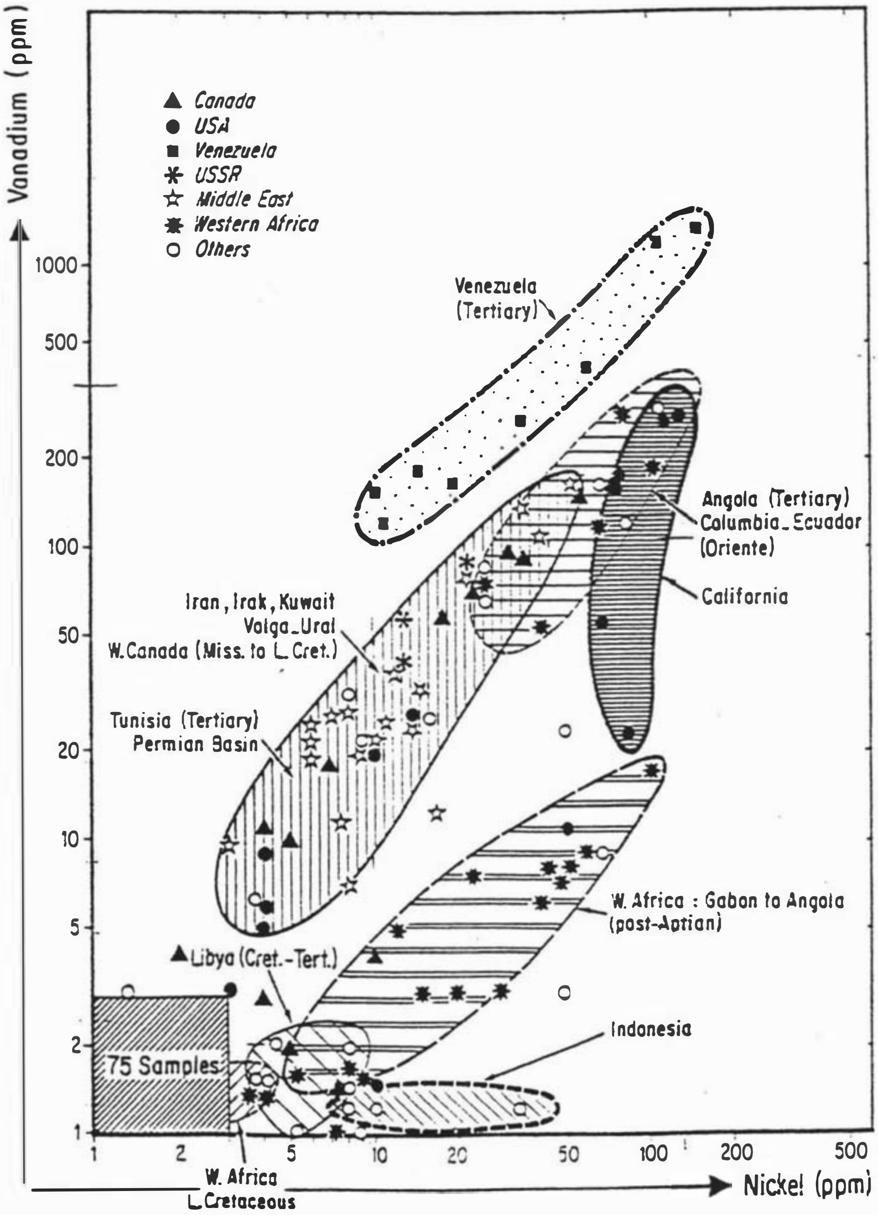
[1] Biomarkers (biological markers) are compounds in petroleum and rock extracts which can be unambiguously linked to natural products of biological origin and are largely unaltered by chemical and physical processes. The most common biomarkers include alkanes (derived from landplant waxes and fatty acids), porphyrins (derived from chlorophyll or haemoglobin), and steranes and triterpanes (derived from steroids and terpenoids).

Hodgson (1954) studied V, Ni and Fe concentrations in crude oils from Alberta Basin, Canada to gain information about maturation, migration and accumulation of these oils. He concluded that maturation and degradation have a major effect on the trace element content of oils and that the V/Ni ratio declined with increasing age of the oils. Data examined in a second study on Alberta crude oils indicated that the distance of migration is reflected in the V and Ni content of the oils (*Hodgson and Baker 1959).* The workers suggested that the adsorption of polar material on to rock grains during migration was responsible for the lower metal content in migrated oils.

Most studies focussed on Ni and V, as these two elements occur in relatively high concentrations in most marine oils. The concentrations of Ni and V can vary from less than 1 µg/g up to 1200 µg/g V and 150 µg/g Ni (*Tissot* and *Welte 1984).* Ni and V can be successfully used to distinguish between oils from different geographical areas as shown by *Tissot* and *Welte (1984)* (Figure 1). As Ni and V concentrations can be related to source rock type and depositional environment (*Barwise 1990)*, these elements have been used in oil-oil and oil-source rock correlations and in the study of hydrocarbon migration patterns.

Barwise (1990) examined the Ni and V content of oils derived from marine and terrestrial source rocks and divided the samples into different classes according to their origin and kerogen type. The study showed that oils could also be classified based only on API gravity, S content and/or their respective V and Ni concentrations. Oils derived from source rocks with low clay content and high organic sulphur content, such as carbonate rocks, contained high Ni and V concentrations. Crude oils sourced by marine shales or lacustrine rocks showed only moderate quantities of these two metals, whereas land plant-derived oils contained small amounts of the elements. Terrestrial crude oils sourced by lacustrine rock differed from other land plant-derived oils, as their Ni/V ratios are usually greater than 2, with some Chinese oils showing Ni/V ratios greater than 10. The concentration of Ni and V varied strongly with the maturity of oils and high maturity crude oils contained only small amounts of Ni and V, even if they originated from marine source rocks.

Figure 1: Nickel and V content in oils from various origins (after Tissot and Welte 1984)



Vanadium and Ni contents of 175 crude oils from various origins. The <u>shaded area</u> contains 75 crude oils of paraffinic, naphthenic, or paraffinic-naphthenic types (after Tissot and Welte 1984).

The Ni and V concentrations and Ni/V ratios could be useful correlation parameters for oils but only if the elements are present in measurable amounts. Low elemental concentrations are subject to large errors and could not be used with confidence *(Barwise 1990)*.

Al-Sharistani and *Al-Atyia (1972)* measured V and Ni concentrations in crude oils from three oilfields in Iraq to determine if the oils had the same source and if vertical migration of the oils had taken place. They based their study on the assumption that the V and Ni concentrations and V/Ni ratios in oils derived from a common source which had not migrated far would be very similar. If some oils had migrated extensively, then their respective trace element contents would be lower than concentrations in the unmigrated hydrocarbons. The V/Ni ratio, though, should be similar in migrated and unmigrated oils. The study showed distinct differences in V and Ni concentrations, but similarities in their V/Ni ratios. *Al-Sharistani* and *Al-Atyia (1972)* concluded that the oils were derived from the same source and that extensive vertical migration of some oils had taken place.

The advances in instrumental methods for the determination of trace elements, especially the application of instrumental neutron activation analysis (INAA), has made possible the quantification of a wide range of elements. Nickel and V, as well as other trace element concentrations could be analysed by advanced statistical methods to obtain information about the origin of oils and their relationship between them.

Hitchon et al. (1975) determined 22 trace element concentrations in their study of Alberta crude oils. The workers concluded that trace element distributions are controlled by oil maturation rather than migration. In a re-evaluation of the data, *Hitchon* and *Filby (1984)* used multiple-discriminant function analysis to group the Alberta crude oils into three families. They used S, Co, V, Se and Br as discriminators and the resulting classification agreed closely with a classification scheme obtained by extensive hydrocarbon and sulphur analysis.

Curiale (1987) determined Cu, Fe, Mn, Ni and V concentrations in North Alaskan crude oils and used cluster analysis to classify the oils into families based on the transition element contents. He concluded that element ratios such as V/(V+Ni) and Fe/V are useful to distinguish different oil types in the area.

Ellrich et al. (1985) studied 12 trace element concentrations in oils from 17 oil fields from Southern Germany and classified the oils into three families based on their Ni, V and S content. They were also able to correlate the iodine content of the oil with the iodine content of formation waters. *Hirner (1987 a, 1987 b)* continued this study and included the trace element content in bitumen, kerogen and asphaltenes. Elements strongly associated with the organic fractions in oils, asphaltenes and kerogen, such as Ni and Co, combined with statistical methods, were successfully used for oil-oil and oil-source rock correlations. The oils could be successfully grouped into families based on differences of the trace element distribution in asphaltenes[1] and maltenes[2].

1.2 AIM OF THE STUDY

Oil exploration in Taranaki Basin, New Zealand, started in 1865 with the drilling of the Alpha oil well near New Plymouth and early prospecting focussed on areas around known oil seepages in Taranaki, on the East Coast near Gisborne and on the West Coast of the South Island. Commercial quantities of hydrocarbons have so far been discovered only in Taranaki Basin, although oil exploration has included all areas of New Zealand.

Geochemical studies of the crude oils from Taranaki Basin showed that the oils were derived from source rocks with significant terrestrial land plant input and that they all have similar maturity levels (*Czochanska et al. 1988)*. Biomarker studies of available well cuttings revealed that these rocks were not thermally mature enough for oil generation and that the source rocks for the Taranaki oils are probably buried at depths of about 5.5 to 6 km (*Cook 1987, Czochanska et al. 1988, Collier 1989, Johnston et al. 1990)*. The oils are very similar in maturity, they are low in sulphur and contain high amounts of aliphatic compounds. Three different families of oils (Moturoa, McKee and Maui Fields) could be identified from variations of the distribution of triterpane biological markers (*Czochanska*

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[1] asphaltenes are polar compounds in crude oils which are insoluble in n-pentane or n-heptane.

[2] oil fractions remaining after the removal of asphaltenes

et al. 1988). No further distinction of the hydrocarbons in Taranaki Basin could be made from organic geochemical methods.

The aim of the present study is to determine trace element concentrations, mainly Ni and V, in New Zealand oils and available rock extracts, using graphite furnace atomic absorption and to study oil-oil and oil-source rock correlations using trace element concentrations and ratios. The trace element content of oils and rock extracts could help to determine which oils are genetically related, classify them into groups and sub-groups and provide additional information about the origin and migration of these hydrocarbons.

Analysis of some Taranaki oils showed that the Ni and V concentrations in these oils were extremely low and at, or below, the limit of detection. The study was extended to include different analytical techniques (INAA and ICP-ES) to allow the determination of a wide range of elements at low concentration levels. The use of different instruments helped to check the accuracy of results, as it made comparison of data possible. Instrumental NAA also enabled the study of trace elements other than V and Ni, which helped to explain the variations in element content in New Zealand oils. The low Ni and V values are subject to relatively large errors limiting their reliable use in any classification scheme.

As this was the first comprehensive study of trace elements in non-marine oils, several marine and terrestrial oils from different geographical areas were included to examine if the extremely low trace element concentrations in New Zealand oils are characteristic for non-marine oils and if similar concentrations occur in oils from other marine and non-marine source rocks. Most previous comprehensive trace element studies had been limited to one basin or area, and only Ni and V had been used for comparisons of oils of different origins. The oils chosen for comparison included oils derived from shale, carbonate, lacustrine and land plant source rocks with maturity levels ranging from low to high. The asphaltene fractions of New Zealand and some overseas oils were analysed to determine the enrichment of elements in the organic fractions. Metals are bound very strongly to organic compounds in the asphaltene fraction, and maturation and migration should have a lesser effect on their content. The asphaltene fractions might also be less affected by contamination of minerals and could possibly supply better information about the relationship of Taranaki oils.

The study was designed to supply information about trace element concentrations and distributions in oils and condensates of the Taranaki Basin. The data could help to shed more light on the migration paths and genetic relationship of these hydrocarbons and perhaps confirm a common source. The collected trace element concentrations would also allow a comparison with other terrestrial, lacustrine and marine sourced oils and will show how similar or different crude oils mainly generated by coal are to other land plant-derived oils. Variations in trace element concentrations might allow for discrimination of oils with distinct marine influence and could also reflect differences in maturity levels.

II. PETROLEUM GEOLOGY AND GEOCHEMISTRY

2.1 OIL FORMATION AND ACCUMULATION

Petroleum is formed through a complex series of events which have been separated into three geochemical stages - diagenesis, catagenesis and metagenesis - based upon the different biological, chemical and physical processes occurring as a result of increasing thermal stress. Table 2.1 is a short summary of reactions taking place during the thermal evolution of organic matter in sediments, and the nature of the resultant organic matter.

2.1.1 DIAGENESIS, CATAGENESIS, METAGENESIS

A. Diagenesis

Sediments rich in organic matter are most often deposited in shallow marine or lacustrine environments with good supply of organic matter, medium sedimentation rate, and quiet and anoxic bottom waters. Such favourable conditions are found in estuaries or lagoons on the continental shelf, deep sea basins with restricted water circulation, and swamp and lacustrine environments on land.

The organic matter is deposited as dead or living organic particulates, dissolved organic compounds and organic matter adsorbed on to mineral matter such as clay particles. Sediments can only be preserved and concentrated under certain conditions. The burial has to be rapid, to ensure that the organic matter is not exposed to the surrounding atmosphere for long. The oxygen supply must be limited to avoid complete degradation of the organic matter by chemical or microbial processes. High productivity and rapid decay of organic matter may produce an environment with low oxygen concentration sometimes accompanied by the presence of anaerobic bacteria.

The transformation of organic matter to kerogen during diagenesis involves a series of complex processes, which are described in detail by *Tissot* and *Welte (1984)*.

Table 2.1: Evolution of sedimentary organic matter

MATURATION STAGE	REACTIONS	RESULT
Early Diagenesis	<50°C: Microbial activity, hydrolysis, conversion of biopolymers to monomers.	During Diagenesis: Kerogen[1] formed small amounts of biomarkers persist from original organic matter (bitumen[2]).
Late Diagenesis	<50°C: Polycondensation, polymerization, and insolubilization forming large organic molecules. (geopolymer=kerogen) Loss of carboxylic acid groups.	
Catagenesis	about 50 to 150°C: Thermal degradation of kerogen. Principal stage of oil formation. Breaking of carbon-carbon bonds in chains and saturated cycles.	Crude oil and gas formed. (heavy oils→light oils→condensate→wet gas).
Metagenesis	>200°C: Random and frequent thermal cracking of carbon-carbon bonds. Aromatic layers in kerogen form large clusters.	Some gas formed. Kerogen is altered to highly aromatic structure. Breakdown of oil to gas

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[1] Kerogen: Organic matter in sedimentary rock which is insoluble in organic solvents

[2] Bitumen: Organic matter in sedimentary rock which is soluble in organic solvents

The reactions occurring during the first stage of burial include the degradation of molecules such as proteins, carbohydrates and lipids into separate amino acids, sugars and fatty acids by microorganisms (*Tissot* and *Welte 1984*). These reactions take place at shallow depth and low temperatures.

The second stage involves polycondensation and polymerization of these chemicals to large molecules comparable to fulvic and humic acids. Further condensation and the loss of heavy NSO-compounds and functional groups (such as the carboxylic acid group) lead to increased insolubility. All these processes occur at burial depths of no more than several hundred metres, at low pressure and at temperatures below 50°C. The resulting organic matter is mainly composed of kerogen, but also contains a small amount of biomarkers. Biological markers are compounds in petroleum and source rock extracts largely unaltered by chemical and physical processes and can be linked to natural products of biological origin.

Tegelaar et al. (1989) however, proposed an alternative and simple mechanism of kerogen formation, based on the selective preservation of biological macromolecules as observed in coal macerals. Their electron microscopy studies showed the existence in kerogen of various biological structures (such as cell walls) which are directly inherited from phytoplankton or bacteria. They suggested that at least part of the kerogen might be derived from the selective preservation of resistant biomacromolecules.

B. Catagenesis

During further burial of the sediment, the kerogen is subjected to increased temperature and pressure. The main stage of petroleum formation starts at temperatures above 50°C.

During catagenesis, the higher temperature provides the energy necessary to break the carbon-carbon bonds in chains and saturated cyclic compounds (*Philippi 1965)*. The thermal cracking is possibly catalysed by mineral matter. Gas and hydrocarbons with low and medium molecular weight are formed. The permeability and porosity of the rock unit decrease and water is expelled from the pores.

The amount and type of hydrocarbons produced during this stage depend strongly on the type of organic matter and the temperature versus time relationship (*Waples 1988)*. The depth of oil formation varies between different basins as it depends on the geothermal gradient, the duration of the burial and the nature of the organic matter.

In the later stage of catagenesis, when temperatures of about 200°C are approached, more frequent and random cracking of carbon bonds occurs, resulting in the formation of gas and condensates.

C. Metagenesis

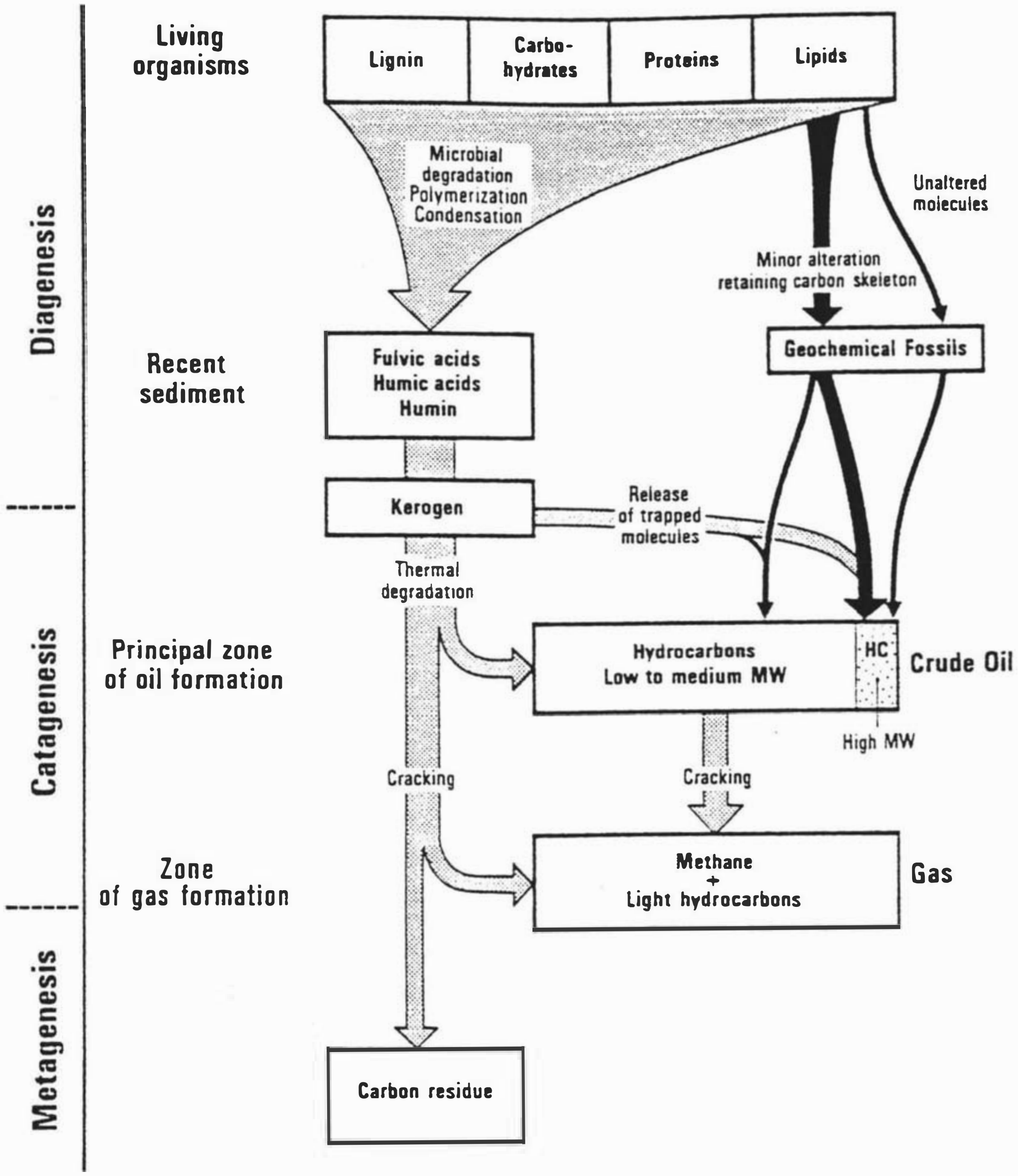
The last stage in the thermal evolution of organic matter is metagenesis, which takes place at greater depth where temperatures are above 200°C.

Gas is produced by the breakage of carbon bonds in previously formed hydrocarbons, and the cracking of kerogen bonds. In this last stage, the organic matter is thermally altered and kerogen is structurally rearranged to a highly ordered and aromatic structure. Figure 2 summarizes the occurring reactions and processes.

2.1.2 KEROGEN

Kerogen is defined as that part of the organic matter in sedimentary rock that is insoluble in organic solvents (*Durand 1988)*. Bitumen is organic matter soluble in organic solvents and contains "free" hydrocarbons, asphaltenes and resins, that have been formed during geological processes (*Durand 1988)*.

Figure 2: Formation of petroleum from sedimentary matter (after Tissot and Welte 1984)



Four kerogen types have been distinguished using optical examination and physical and chemical analysis. The classification is based upon chemical composition (C, H, O and N), physical structure and petroleum-generating potential (*Tissot* and *Welte 1984, Durand 1988).*

Type I Kerogen has a high initial H/C ratio and contains a large amount of aliphatic chains. It is mainly derived from algal lipids or from organic matter which has been severely biodegraded. This type of kerogen has a high potential for gas and oil generation but is not very common and occurs mostly in lacustrine environments.

Type II Kerogen is mainly derived from marine organic matter which was deposited in a reducing environment. It contains more aromatic and naphthenic compounds than Type I kerogen, and has medium to high sulphur concentrations. This type of organic matter is found in many oil shales and is the most frequently found source for oil. Its oil generating potential is lower than observed for Type I kerogen, but is still very significant.

Type III Kerogen has a low initial H/C ratio, but a high atomic O/C ratio. It is mainly derived from terrestrial plant material and has only a limited potential for oil generation. It may generate abundant gas if the organic matter is heated to sufficient temperatures. Coal shows chemical and evolutionary similarities to Type III and both are formed under less reducing conditions than Kerogen I and II (*Filby* and *van Berkel 1987).* Coal can generate commercial quantities of oil if its liptinite content is high enough (*Tissot* and *Welte 1984).* Liptinite is defined as the maceral group derived from organic matter high in lipids. Macerals are coalified plant remains found in organic sedimentary rocks.

Type IV Kerogen consists of highly oxidised organic matter containing an abundance of aromatic structures and no aliphatic chains. It shows no hydrocarbon generating potential (*Tissot* and *Welte 1984).*

Most kerogens fall in one of these groups although the composition of kerogen can vary among one type. The variability of contributing organisms, such as mixtures of terrestrial and marine inputs and the degree of preservation, are the main reasons for these variations.

2.1.3 TRACE ELEMENTS IN CRUDE OILS

Crude oils contain varying amounts of trace elements. The two most common and abundant metals found in petroleum are nickel and vanadium. A great range of other trace elements can be detected in oils, but only Ni and V occur in appreciable amounts. The highest concentrations of these two elements have been recorded in Venezuelan crude oils, which contain up to 1200 µg/g V and 150 µg/g Ni (*Tissot* and *Welte 1984)*. Generally, concentrations of both of these elements increase directly with the asphaltic content of the crude oils. Other elements can be present in varying amounts ranging from less than 1 ng/g to more than 100 µg/g (*Filby 1975*).

The amounts of Ni and V vary strongly with the origin of oil. *Hodgson (1954)* concluded that the V/Ni ratio decreases with increasing age of the source rock and that this ratio is altered mainly by degradation, but this conclusion is quite different ot other studies. Other attempts to correlate the Ni/V ratios in oils with age ended in conflicting results (*Filby* and *van Berkel 1986)*.

A recent study by *Lewan (1984)*, however, showed that the V/Ni ratio can withstand weathering, high temperatures, water washing, microbial degradation and oxidation without changing. He suggested that the ratio depends on composition of the source rock. Some of the metal diffuses into the source rock from the overlaying water column with concentration continuing until all possible complexing sites are filled. The proportionality then remains fixed from this point on. The ratio of V to Ni and the sulphur concentration depend on the depositional environment of the source rock and it varies with pH, Eh and sulfide activity at the time of deposition.

The trace elements found in oil exist in a variety of complexes and forms (*Yen 1975)*. The most important complexes are the metallo-porphyrins, which were first identified in petroleum, bitumen and coals by *Treibs (1934)*. Porphyrins are derived from plant chlorophyll (or animal haemoglobin) which is degraded during the thermal formation of petroleum. Only Ni and V have been identified in porphyrin complexes with both elements bound as bivalent cations (Ni^{2+} and VO^{2+}). The bonding of V and Ni to the porphyrin complexes probably occurs during diagenesis (*Yen 1975*), but it is not clear if this occurs in the water column, at the water sediment boundary or within the sediment (*Quirke 1987)*.

Fish et al. (1984) found that over 90% of the Ni in heavy crude oils and asphaltenes was present in the non-porphyrinic form. They explained this fact as due to the greater stability of the V porphyrin complex and that the vanadyl ion replaces the nickel cation.

A varying percentage of V, Ni and all other trace elements occurs in non-porphyrinic form. The structure of the non-porphyrinic complexes is mostly unknown, as identification by chromatography is extremely difficult due to the complex matrix of the heavy oil fractions.

The asphaltene and resin fractions of oils contain most of the trace elements (up to 90%) (*Zaki et al. 1989)*. Asphaltenes are stacked aromatic sheets of high molecular weights. The structure of the resin fraction is comparable to the asphaltenes although the resins are slightly less aromatic and contain free esters, acids or ethers and high amounts of heteroatoms (*Yen et al. 1961*). The trace elements are probably directly bound to heteroatoms in the asphaltenic fraction or exist as degraded metallo-porphyrin complexes associated by π-π bonds to the aromatic sheets *(Yen 1975)*. Other possibilities are the existence of carboxylic acid salts, organometallic compounds of Hg, As and Sb or inorganic matter such as colloidal minerals (NaCl, silica, clay).

Heavy crude oils show good correlation between the sulphur content and the V concentration. Both can be simultaneously eliminated when the oil is treated with water. *Tissot* and *Welte (1984)* suggest therefore, that V is mainly bound to chemical structures containing sulphur.

2.1.4 ORIGIN OF TRACE ELEMENTS IN OIL

How and when trace elements are introduced into crude oils is still an unanswered question. They might have originated from the original biological matter, could have replaced other metals in the asphaltene fraction or could have been incorporated from solid or aqueous phases during maturation or migration. Most workers, however, agree that the metals originate in the source rock and that the introduction of metals during migration is highly unlikely (*Hodgson* and *Baker 1959*).

All plants and animals require trace elements in certain amounts and elements are present in varying concentrations which depend on the type of organism and its environment. It is known that some marine organisms, such as tunicates, are able to concentrate V as haemovanadin and that is considered to be one of the sources of the element in petroleum derived from marine organic matter (*Yen 1975*). Some plants are able to concentrate certain trace metals under the right conditions (e.g. *Brooks* and *Wither 1977)* and can tolerate high levels of otherwise toxic elements.

A comparison of some elements in dry tissues from land and marine plants (*Mason* and *Moore 1982*) shows relatively few differences in the concentrations. Br, Fe, I, Na, Sr and S are the elements found in significantly higher concentrations in marine plants. Aluminium and Mn seem to be two elements enriched in land plants. The major elements found in petroleum - vanadium and nickel - occur in comparable concentrations in marine and land plants.

Lewan and *Maynard (1982)* studied the enrichment of V and Ni in the bitumen of organic sedimentary rocks. This enrichment is only observed in Type I and Type II kerogen which can be explained by the rapid decomposition of chlorophyll from higher land plants. The destruction of the chlorophyll before deposition prevents the formation of the highly stable porphyrin complexes which are partly responsible for the occurrence of high Ni and V concentrations in oils.

Lewan and *Maynard (1982)* investigated two possibilities for Ni and V enrichment in organic sediments: the accumulation of V and Ni endemic to organic matter, and the diffusion of the elements from interstitial, connate water in the sediments. As the maximum endemic concentrations of Ni and V in marine organisms are 32 µg/g and 45 µg/g respectively, they assumed that another source had to exist to supply the higher amounts of V and Ni measured and concluded that this enrichment was influenced by two factors. Chlorophyll structures have to be preserved by deposition of the organic matter under anaerobic conditions, and the sedimentation rate has to be slow enough to allow the persistence of an open water column to supply sufficient trace metals. *Filby* and *van Berkel (1987)* suggested that clay-mineral surfaces in deeper buried sediments are an additional source of metal ions.

Only V and Ni porphyrin complexes have been studied extensively and little information about the incorporation and complexing of other trace metals and non-porphyrinic Ni and V complexes is available.

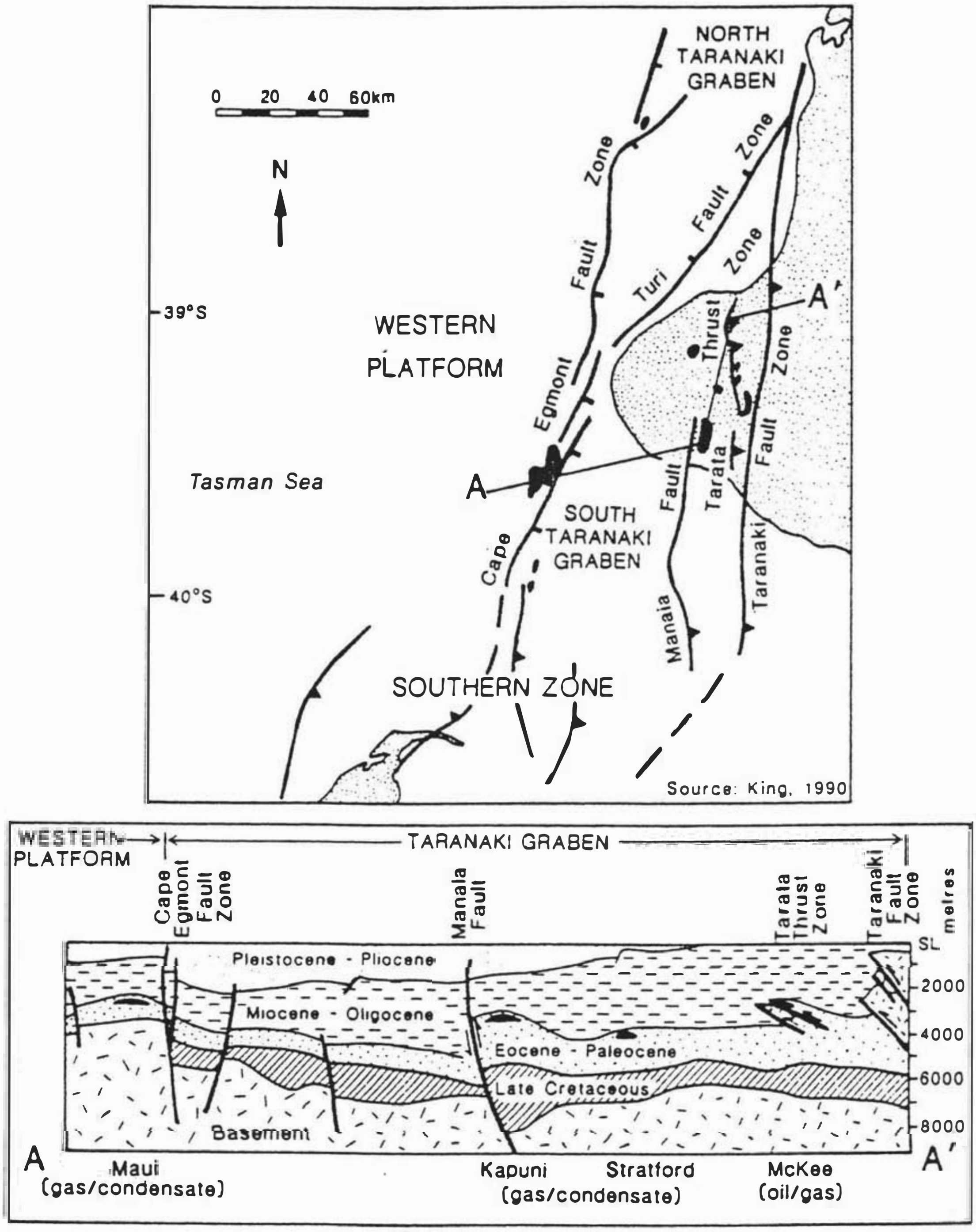
2.2 NEW ZEALAND OILS

The Taranaki Basin is the only commercial hydrocarbon- producing region in New Zealand. All major occurrences of gas, condensates and oil have been discovered in this area since oil exploration began in 1865.

2.2.1 GEOLOGY OF TARANAKI BASIN

Taranaki Basin lies along the west of the central North Island and includes the Taranaki Peninsula. The basin deepens towards the north and northeast and shallows towards the south and west. The Taranaki Boundary Fault forms the eastern margin. *Pilaar* and *Wakefield (1984)* subdivided the basin into two main regions: the Taranaki Graben and the Western Platform. *King (1990)* divided the Basin into five main structural provinces: the Western Platform, Southern Zone, South Taranaki Graben, North Taranaki Graben and Tarata Thrust Zone. A map of Taranaki Basin and a structural cross-section is shown in Figure 3.

Figure 3: Structural subdivision and structural cross-section of the Taranaki Basin (after King 1990)



Source: King, 1990

The structural evolution of Taranaki Basin took place in four phases between the middle Cretaceous and Pleistocene *(King* and *Robinson 1988, King 1990).* The different events are the direct and indirect results of movement of the Australian and Pacific plates. The structure of the Taranaki Graben was formed by subsequent or combined phases of rifting, subsidence and compression from the middle Cretaceous onwards (*Pilaar* and *Wakefield 1984, Knox 1982, Ministry of Commerce 1992, King 1990, Cook and King 1987).*

Sedimentation in Taranaki Basin happened in three main stages. During the Late Cretaceous, mainly fluvio-lacustrine sediments (Pakawau Group) were deposited in sub-basins created by regional faulting. Later, different regional sedimentation patterns occurred. Terrestrial sedimentation prevailed in the south and east, whereas mainly marine sediments were deposited in the northern and western parts of the basin. These were followed by marine sedimentation throughout most of the basin. During the last stage, from Early Miocene onwards, major uplifts resulted in increased terrestrial sedimentation (*King 1990, King* and *Robinson 1988, Geosearch 1991, Ministry of Commerce 1992).*

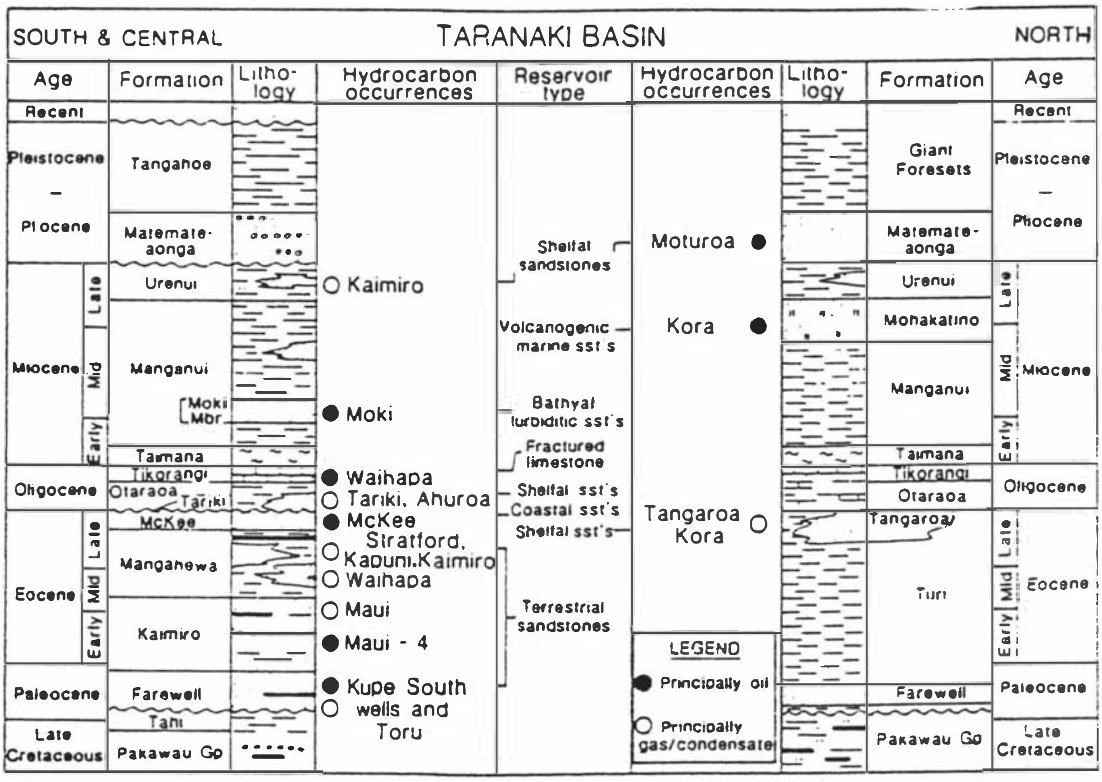
Sandstone formations of the upper Kapuni Group were for a long time seen as the major reservoir rocks in the Taranaki Basin. Recent discoveries have shown that hydrocarbon reservoirs can also occur in younger sandstone and fractured limestone formations (along the Tarata Thrust line) and volcanoclastic sediments (one of the Kora oil reservoirs). Figure 4 shows hydrocarbon accumulations under production or development.

2.2.2 ORGANIC GEOCHEMISTRY

Extensive organic geochemistry has examined the nature, origin and possible source rocks of New Zealand oils.

Cook (1987, 1988) summarised and interpreted geochemical data for oils from the western part of New Zealand. Oils from Taranaki Basin are generally very waxy and low in sulphur (<0.01%), indicating a mainly terrestrial source (*Tissot* and *Welte 1984).* The

Figure 4: Hydrocarbon accumulations under production or development (after Geosearch 1991)



chain length of the n-alkanes in the oils of up to C_{35} is characteristic of a source containing leaf waxes of terrestrial plants.

Biomarkers such as isoprenoids, steranes and triterpanes are useful in identifying the type of source rock, the depositional environment and the maturation level of petroleum. Pristane and phytane are two isoprenoid compounds derived from the side chains of chlorophyll. The pristane to phytane ratio is used as an indicator for the depositional environment as pristane is formed under oxidising conditions, whereas the formation of phytane occurs mainly in a reducing environment. The pristane to phytane ratio in Taranaki oils, together with the high abundance of n-alkanes, indicates a highly oxic nearshore marine-open peat swamp environment which incorporated a large amount of landplant organic matter. The presence, amount and proportion of certain triterpane and sterane biomarkers confirmed terrestrial kerogen derived from higher plant organic matter as the source (*Czochanska et al. 1988)*. Generally, Taranaki oils show a biomarker profile similar to oils from Gippsland and the Mahakam Delta, although lower levels of triterpanes point to a contribution of organic matter from a paralic sedimentation environment. The abundance of certain sterane isomers also suggests the generation of the oils from clay minerals, as clay minerals are believed to act as catalysts in the rearrangement of sterol and sterene to the sterane isomers. Results based on studies of the extent of side chain isomerisation of biomarkers also showed that the oils are generated from mature source rocks and the maturity level is equivalent to a vitrinite reflectance of about 1% (*Czochanska et al. 1988)*. Vitrinite is derived from lignified tissues of higher land plants and is present in coal and kerogen. The reflectance of polished vitrinite particles increases with progressing aromatization and is used as a maturation parameter. Source rocks are mature to produce oil at vitrinite reflectances between 0.5% and 1.3 % (*Tissot* and *Welte 1984*).

Carbon and sulphur isotope studies (*Hirner* and *Lyon 1989* and *Hirner* and *Robinson 1989*) of oils and source rock samples indicated that West Coast, Maui and Nelson coals might be possible source rocks. That study supported a terrestrial source, but carbon isotope results indicated a varying degree of marine influence. None of the oils seem to be biodegraded and GC-MS studies could not differentiate between oils generated from the Kapuni or Pakawau groups (*Robertson Research 1984*). Biomarker and isotope studies indicate that they all belong to one family and the small variations encountered are probably due to minor differences in the source material (*Robertson Research 1984*).

Possible source rocks lie within the Kapuni Group or the Late Cretaceous Pakawau Group. *Cook (1987)* and *Johnston et al. (1990)* suggested that perhydrous coals formed during the Late Cretaceous are the source of the Taranaki oils. As the maturity level of available and studied source rocks is too low, source rocks generating oil are probably buried below 5.5 km (*Cook 1987*) and drilling has not yet reached them. These great depths limit oil generation to the central graben. New seismic studies show several distinct basins within the graben area (*Thrasher 1992*) and oil found outside this region possibly had to migrate to the existing reservoirs.

Although caution is recommended by *Moldowan et al. (1988)* in using some of the geochemical parameters in distinguishing between marine and non-marine oils, the combined results clearly indicate a non-marine source. The kerogen was deposited in a freshwater swamp environment with input of higher land plant matter. The source rocks are probably buried at a depth of 5.5 to 6 km, with most oils migrating some distance vertically and probably horizontally to their reservoirs.

2.2.3. SAMPLES

All New Zealand samples (except two seep oils from the East Coast Basin) were collected from the national petroleum archive curated by the Institute of Geological and Nuclear Sciences (Wellington). East Coast seep oil, oilsand and rock samples were obtained from K.Rogers, J.D.Collen and D.Francis. Overseas samples were supplied by Exxon Research Company (Houston, Texas, USA) and Shell Research BV.(Rijswijk, Netherlands). Pritchard bitumen and bitumen carbonaceous shale samples were provided by J. Clayton, Petroleum Geology, United States Geological Survey (Denver, Colorado, USA). B.Luo (Lanzhou, China) supplied oil samples from the Yumen oilfields, and J.D.Collen, Research School of Earth Sciences, Victoria University, Wellington provided other Chinese oil, oilsand and rock samples. The Australian oils from the Cooper/Eromanga Basin were supplied by Santos Ltd. (Adelaide, Australia). BP New Zealand Ltd. (Wellington) provided a sample of Saudi Arabian light crude oil. A complete sample list with literature references is given in Table 2.2.

A. Taranaki Basin

Oil seeps occur at a number of localities in New Zealand and many areas have been explored for hydrocarbon accumulations. Until now, commercial quantities of hydrocarbons have been discovered only in Taranaki Basin and this region is currently regarded as the most prospective in the country.

Taranaki Basin is mainly a gas/condensate producing area but many wells have yielded varying amounts of crude oils although not always in commercial quantities. Figure 5 gives a summary of the main hydrocarbon-producing fields and wells in the basin.

Thermal maturity, hydrogen index and biomarker studies indicate the Cretaceous coal measures in the Kapuni and Pakawau groups as potential source rocks (*Cook 1987, Johnston et al. 1990, Collier 1989*), with most gas and oil reservoirs located in the upper Kapuni sequences. The Paleocene-Eocene Kapuni Group and the similar underlying Late Cretaceous Pakawau Group are sequences comprising sandstone, siltstone, carbonaceous shale and coal seams up to 7 m thick (*King* and *Robinson 1988*). Figure 6 shows a stratigraphic map of Taranaki Basin.

Hydrocarbon reservoir rocks are mostly terrestrial-paralic-nearshore sandstones in the Kapuni Group (e.g. McKee, Maui, Kupe South). Other proven reservoir rocks include the Miocene turbidite sands in the Moki and Ngatoro fields, the Matemateaonga Formation in the Moturoa Field, the fractured Tikorangi Limestone in the Waihapa Field and volcanic rocks and volcanoclastic sediments in the North Taranaki Graben (Kora Structure) (*Geosearch 1991*).

Table 2.2: Complete sample list

COUNTRY	BASIN	FIELD OR SEEP	WELL	SUPPLIER	GENERAL REFERENCE
New Zealand	Taranaki	Kaimiro	Kaimiro-1A	all New Zealand samples were supplied by the petroleum archive curated by the Institute of Geological and Nuclear Sciences	Taranaki Basin: Cook 1987, Hirner and Lyon 1989, Hirner and Robinson 1989, Ministry of Commerce 1992, Geosearch 1990 King and Robinson 1988, King 1990, Czochanska 1988, Johnston et al. 1990 Robertson Research 1984
New Zealand	Taranaki	Kapuni	Kapuni-1		
New Zealand	Taranaki	Kora	Kora-1, DST2		
New Zealand	Taranaki	Kora	Kora-1, DST3		
New Zealand	Taranaki	Kupe	Kupe South-1		
New Zealand	Taranaki	Kupe	Kupe South-2		
New Zealand	Taranaki	Kupe	Kupe South-3		
New Zealand	Taranaki	Kupe	Kupe South-4		
New Zealand	Taranaki	Kupe	Kupe South-5		
New Zealand	Taranaki	Kupe	Toru-1		
New Zealand	Taranaki	Maui	Maui-1		
New Zealand	Taranaki	Maui	Maui-3		
New Zealand	Taranaki	McKee	McKee-1		
New Zealand	Taranaki	McKee	McKee-2		
New Zealand	Taranaki	McKee	McKee-3A		
New Zealand	Taranaki	McKee	McKee-4		
New Zealand	Taranaki	McKee	Pouri-1		
New Zealand	Taranaki	McKee	Pukemai Cond.		
New Zealand	Taranaki	McKee	Pukemai-1B		
New Zealand	Taranaki	McKee	ToeToe-1		
New Zealand	Taranaki	McKee	ToeToe-2B		
New Zealand	Taranaki	McKee	ToeToe-3		
New Zealand	Taranaki	McKee	ToeToe-4		
New Zealand	Taranaki	McKee	Tuhua-1		
New Zealand	Taranaki	McKee	Tuhua-2 A-Sand		
New Zealand	Taranaki	McKee	Tuhua-2 B-Sand		
New Zealand	Taranaki	Moki	Moki-1		
New Zealand	Taranaki	Moki	Maui-4		
New Zealand	Taranaki	Moturoa	Moturoa-1		
New Zealand	Taranaki	Moturoa	Republic-1		
New Zealand	Taranaki	Moturoa	Republic-4		
New Zealand	Taranaki	Moturoa	Taranaki-5		
New Zealand	Taranaki	Tariki	Ahuroa-2		
New Zealand	Taranaki	Tariki	Tariki-1		
New Zealand	Taranaki	Tariki	Tariki-1A		
New Zealand	Taranaki	Stratford	Stratford-1		
New Zealand	Taranaki	Waihapa	Waihapa-1		
New Zealand	Taranaki		Pukearuhe-1		
New Zealand	Taranaki		Urenui-1		
New Zealand	Rotorua	Seep	Waiotapu		
New Zealand	East Coast	Seep	Waitangi	D. Francis, K. Rogers, Wellington	Ministry of Commerce 1992, Geosearch 1990
New Zealand	Westland	Seep	Kotuku		Ministry of Commerce 1992, Geosearch 1990
New Zealand	Murchison		Blackwater-1		Ministry of Commerce 1992, Geosearch 1990
New Zealand	Canterbury		Galleon-1		Ministry of Commerce 1992, Geosearch 1990

COUNTRY	BASIN	FIELD OR SEEP	WELL	SUPPLIER	GENERAL REFERENCE
Australia	Cooper/Eromanga		Alwyn-1	all oils from the Cooper/Eromanga Basin were supplied by Santos Ltd., Adelaide South Australia	Cooper/Eromanga Basin: Kantsler et al. 1984
Australia	Cooper/Eromanga		Bagundi-1		
Australia	Cooper/Eromanga		Big Lake-37		
Australia	Cooper/Eromanga		Brumby-2		
Australia	Cooper/Eromanga	Dullingari	Dullingari-29, Namur Sst.		
Australia	Cooper/Eromanga	Dullingari	Dullingari-29, Murta Member		
Australia	Cooper/Eromanga	Gidgealpa	Gidgeapla-16		
Australia	Cooper/Eromanga	Gidgealpa	Gidgealpa-17		
Australia	Cooper/Eromanga	Gidgealpa	Gidgeapla-20, Top Namur Sst.		
Australia	Cooper/Eromanga	Gidgealpa	Gidgealpa-20, Birkhead Fm.		
Australia	Cooper/Eromanga	Lepena	Lepena-1, Epsilon		
Australia	Cooper/Eromanga	Lepena	Lepena-1, Patchawarra Fm.		
Australia	Cooper/Eromanga	Meranji	Meranji-1, Namur Sst.		
Australia	Cooper/Eromanga	Meranji	Meranji-1, Patchawarra Fm.		
Australia	Cooper/Eromanga	Merrimelia	Merrimelia-6, Hutton Sst.		
Australia	Cooper/Eromanga	Merrimelia	Merrimelia-6, Murta Member		
Australia	Cooper/Eromanga	Merrimelia	Merrimelia-6, Namur Sst.		
Australia	Cooper/Eromanga	Merrimelia	Merrimelia-12		
Australia	Cooper/Eromanga	Spencer	Spencer-5, Birkhead Fm.		
Australia	Cooper/Eromanga	Spencer	Spencer-5, Mid Namur Sst.		
Australia	Cooper/Eromanga	Strzelecki	Strzelecki-3		
Australia	Cooper/Eromanga	Strzelecki	Strzelecki-5		
Australia	Cooper/Eromanga	Strzelecki	Strzelecki-10		
Australia	Cooper/Eromanga		Taloola-1		
Australia	Cooper/Eromanga		Tantanna-1		
Australia	Cooper/Eromanga	Wancoocha	Wancoocha-2, Birkhead Fm.		
Australia	Cooper/Eromanga	Wancoocha	Wancoocha-2, Murta Member		
Australia	Cooper/Eromanga	Wancoocha	Wancoocha-2, Patchawarra Fm.		
China	Jiuxi	Yaerxia	#114	B. Luo, Lanzhou, China	Juixi Basin: Wang and Coward 1993
China	Jiuxi	Yaerxia	#502	B. Luo, Lanzhou, China	
China	Jiuxi	Yaerxia	#503	B. Luo, Lanzhou, China	
China	Jiuxi	Yaerxia	#506	B. Luo, Lanzhou, China	
China	Jiuxi	Yaerxia	#507	B. Luo, Lanzhou, China	
China	Jiuxi	Laojunmiao	#194	B. Luo, Lanzhou, China	
China	Jiuxi	Baiyanghe	#68	B. Luo, Lanzhou, China	
China	Jiuxi	oilsand	Yumen oilsand	J.D. Collen, Wellington	
China	Minhe		Hutouya	J.D. Collen, Wellington	Bennett (1992)
China	Minhe	oilsand	Minhe Bridge oilsand	J.D. Collen, Wellington	Bennett (1992)
China	Turpan	Yilabu	Toucan-1	J.D. Collen, Wellington	
China	Turpan	Shanshan	Taican-1	J.D. Collen, Wellington	
China	Turpan	Seep	Quiketai	J.D. Collen, Wellington	

COUNTRY	BASIN	FIELD OR SEEP	WELL	SUPPLIER	GENERAL REFERENCE
USA	San Juan	Florence	Florence-6A	J. Clayton, USGS, Denver	San Juan Basin:
USA		Florence	Florence-7A	J. Clayton, USGS, Denver	Clayton et al. 1991
USA			Mansfield-1A	J. Clayton, USGS, Denver	
USA	Los Angeles	Hondo	Hondo-3	Exxon Ltd., Houston, Texas	
USA	Los Angeles	Hondo	Hondo-5	Exxon Ltd., Houston, Texas	
USA	Los Angeles	Hondo	Hondo-7	Exxon Ltd., Houston, Texas	
USA	Los Angeles	Hondo	Hondo-9	Exxon Ltd., Houston, Texas	
USA	Los Angeles	Hondo	Hondo-12	Exxon Ltd., Houston, Texas	
USA	Los Angeles	Hondo	Hondo-22	Exxon Ltd., Houston, Texas	
USA	Los Angeles	Hondo	Hondo-23	Exxon Ltd., Houston, Texas	
USA	Los Angeles	Hondo	Hondo-24	Exxon Ltd., Houston, Texas	
USA	Los Angeles	Hondo	Hondo-29	Exxon Ltd., Houston, Texas	
USA	Los Angeles	Hondo	Hondo-33	Exxon Ltd., Houston. Texas	
USA	Los Angeles	Hondo	Hondo-37	Exxon Ltd.,Houston. Texas	
USA	Williston	Ivanhoe Dome	R.P.Oliver #4 State (22970)	Exxon Ltd., Houston, Texas	
USA	Williston	Big Wall	Texas #1-B Northern Pacific (22966)	Exxon Ltd., Houston, Texas	
USA	Williston	Sumatra	Continental #1 Harris (22971)	Exxon Ltd., Houston, Texas	
USA	Williston	Sumatra	McAlester Fuel Co.#5 Nth Pacific (22974)	Exxon Ltd., Houston, Texas	
USA	Uinta		Alfreda Knudsen-1 (19126)	Exxon Ltd., Houston, Texas	
USA	Uinta	Walker Hollow	Orlan Johnson-1 (21850)	Exxon Ltd., Houston, Texas	
USA	Alaska		Prudhoe Bay	J.D. Collen, Wellington	North 1985
Canada	Alberta	Rainbow	Husky Mobil Rainbow (48101)	Exxon Ltd., Houston, Texas	
Canada	Alberta	Legal	Imperial-Legal	Exxon Ltd., Houston, Texas	
Middle East			OMC 4677	Shell Research, Rijswijk, Netherlands	
Middle East			OMC 5220	Shell Research, Rijswijk, Netherlands	
Middle East			OMC 5363	Shell Research, Rijswijk, Netherlands	
Saudi Arabia		Abquaiq. Abu. Hadriya. Damman Fadhili, Ghawar		BP Ltd., Wellington	
Nigeria			OMC 3813	Shell Research, Rijswijk, Netherlands	
Nigeria			OMC 78	Shell Research, Rijswijk, Netherlands	
Norway	North Sea	Balder	25/11-1 (54051 A)	Exxon Ltd., Houston, Texas	
Norway	North Sea	Balder	25/8-1 (56323)	Exxon Ltd., Houston, Texas	
	North Sea		OMC 4755	Shell Research, Rijswijk, Netherlands	
	North Sea		OMC3168	Shell Research, Rijswijk, Netherlands	
	North Sea		OMC 5217	Shell Research, Rijswijk, Netherlands	

Figure 5: Main hydrocarbon occurrences in Taranaki Basin (after Geosearch 1991)

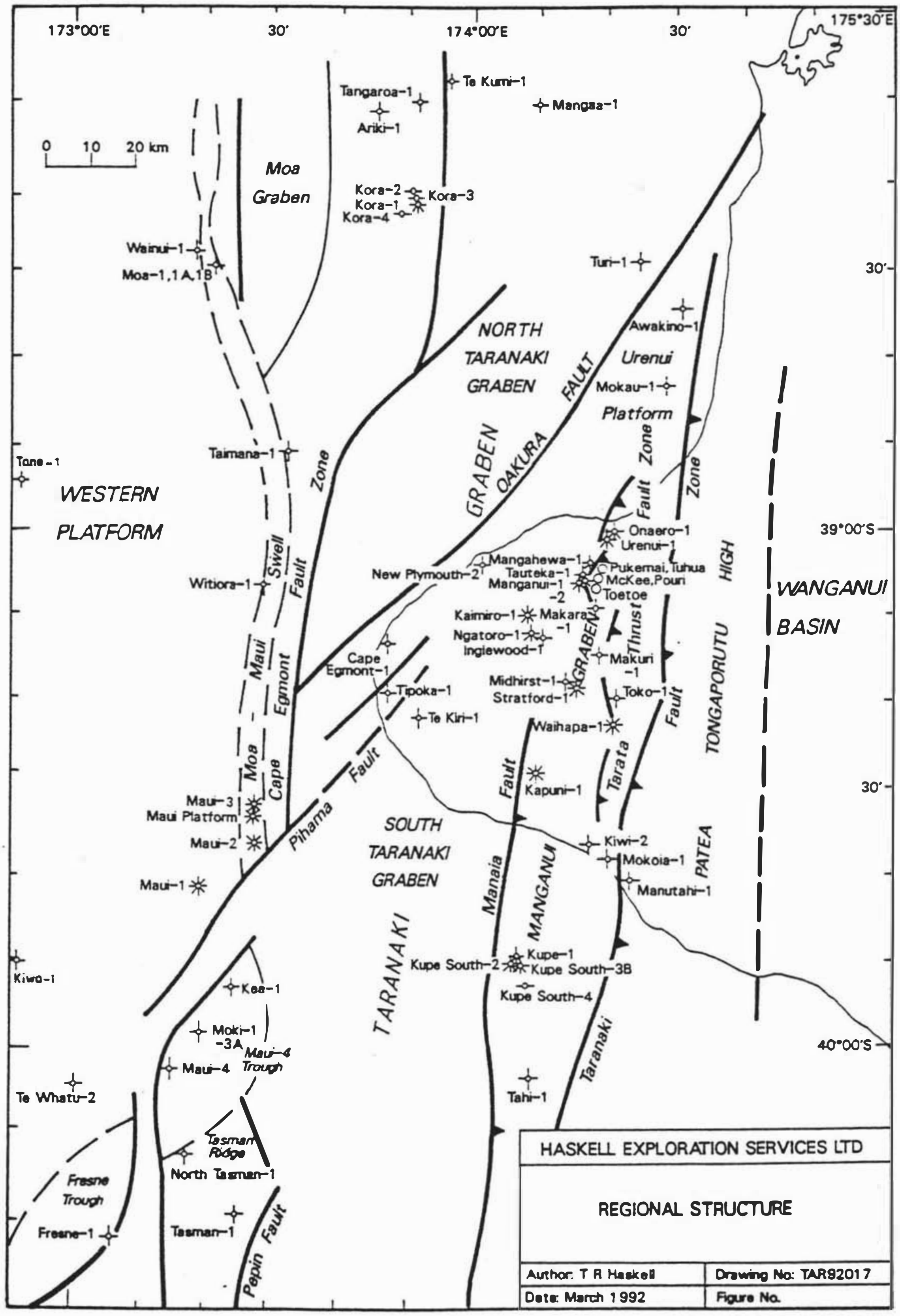
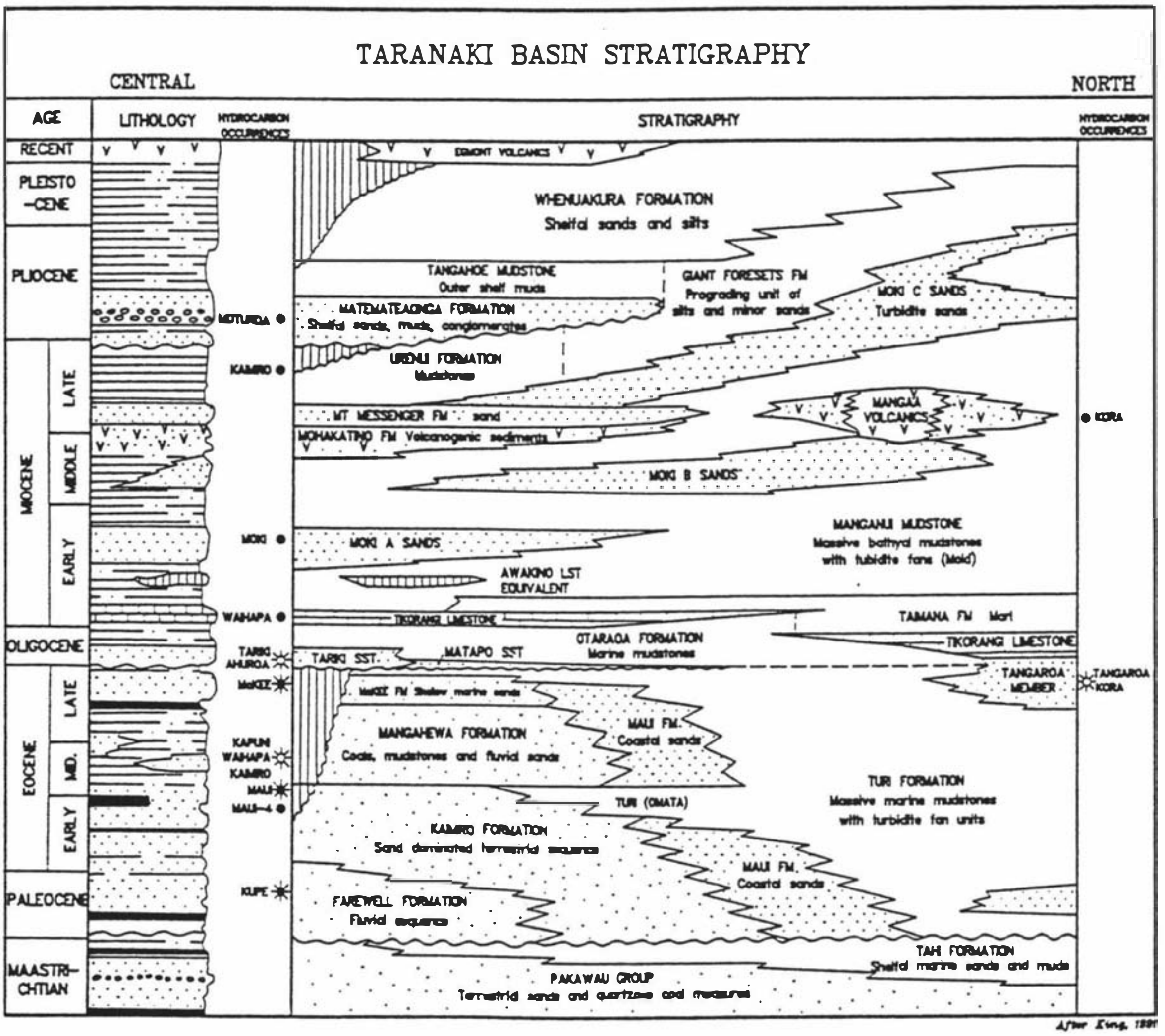


Figure 6: Stratigraphic map of Taranaki Basin (after King 1991)



Many Eocene-age sandstone sequences, like the Mangahewa and the McKee formations, locally contain high amounts of kaolinite (*Ministry of Commerce 1992)*. Porosities of the reservoir sandstones are in the 14% to 18% range.

All oils from the Taranaki Basin are paraffinic with high wax contents (usually above 10%), API[1] gravities of 30°- 45°, relatively high pour points[2] (between 15 and 30°C), very low sulphur concentrations (at or below 0.01%) and low asphaltene contents (from 0 up to 0.3%) (*Cook 1987, Hirner* and *Lyon 1989, Hirner* and *Robinson 1989, Robertson Research 1984*).

Data for the Taranaki oils and other geological information presented below have been collected from different publications and various open file petroleum reports (*Robertson Research 1984, Cook 1987, Hirner* and *Lyon 1989, Hirner* and *Robinson 1989, Geosearch 1991, Ministry of Commerce 1992*). Figures sometimes varied between different studies and the average of the two closest values is reported here.

*** McKee Field**

SAMPLES: McKee-1, McKee-2, McKee-3A, McKee-4, McKee condensate, Pouri-1, Pukemai-1b, Pukemai-2 condensate, Toe Toe-1, Toe Toe-2B, Toe Toe-3, Toe Toe-4, Tuhua-1, Tuhua-2 (A Sand), Tuhua-2 (B Sand)

The structure of the McKee Field is seen as one oil accumulation with two separate gas caps. The oil is produced from the McKee formation, a 40 m to 110 m thick marine sandstone sequence of Late Eocene age overlying the Mangahewa Formation. In the northern area, shale separates the formation into a more productive A sand and a poorer

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[1] American Petroleum Institute measure of the specific gravity of crude oils and condensates. The specific gravity is converted into API gravity by the formula:

$$\frac{141.5}{\textit{spec. gravity at } 16^{\circ}C} - 131.5$$

and API gravity increases with decreasing specific gravity. A light crude oil has API gravity between 35° and 45°.

[2] The pour point of an oil is the lowest temperature at which the crude oil will flow under prescribed, controlled conditions.

B sand. Oils from the McKee field have pour points of around 30°C, average API gravities of 40° and contain about 0.1% sulphur.

*** Kapuni Field**

SAMPLES: Kapuni-1

The hydrocarbon accumulations in the Kapuni Field were found within a main sandstone reservoir below the top of the Kapuni Group, between 3673 and 3810 m. The Kapuni-1 sample has a light yellow colour, a pour point of 19°C and API gravity of 45°. It contains 15% waxy aliphatic compounds and 0.05% sulphur.

*** Maui Field**

SAMPLES: Maui-1, Maui-3 condensate

The Maui field lies offshore and has two distinct reservoirs which are separated by shale and siltstone: Maui A (northeasterly structure) and Maui B (southwesterly structure). The hydrocarbon accumulations are found within the Paleocene to Lower Eocene sands of the Kaimiro group.

The Maui-1 oil sample was produced from the Maui B structure, has an API gravity of 41°, a wax content of about 10%, a sulphur concentration of 0.01% and a pour point of 18°C.

The Maui-3 condensate has a pour point of -25°C, API gravity of 48°, a wax content of 3 % and a sulphur concentration of 0.09%.

*** Kaimiro Field**

SAMPLES: Kaimiro-1 condensate

The Kaimiro-1 condensate reservoir is located between 3611 and 3622 m within the McKee Formation. The condensate has an API gravity of 46°, a moderate pour point and a very low sulphur concentration.

*** Moki Discovery**

SAMPLES: Maui-4, Moki-1

The Maui-4 well was drilled on a separate structure in the same region, before Moki-1. The oil is produced from a 43 m hydrocarbon bearing zone within Eocene age sandstones on top of the Kapuni Group. The oil has an API gravity of 41°, a pour point of 24°C and contains about 15% wax and 0.1% sulphur.

The 22.5 m oil column of the Moki-1 well is located within the Miocene Moki Member sandstone between a 1303.5 m and 1326 m interval. The oil is dark brown, with an API gravity of 37°, contains 20% wax and 0.3% sulphur and has a pour point of 27°C.

*** Tariki and Ahuroa Discovery**

SAMPLES: Tariki-1, Tariki-1A condensate, Ahuroa-2 condensate

The Tariki wells are located on the western side of the Tariki-Ahuroa overthrust. The condensate is produced from the Tariki Sandstone Member with the condensate reservoir lying about 400 m above the Tariki-1 oil column. Tariki-1 encountered good reservoir rocks in the Tariki Sandstone Member and the Kapuni Group, but both were evaluated as water bearing.

The Ahuroa-2 condensate accumulation is found in the Tariki Sandstone Member south of the Tariki-1 well.

*** Kupe South Discovery**

SAMPLES: Kupe South-1, Kupe South-2, Kupe South-3 Kupe
South-4, Kupe South-5, Toru-1

The offshore Kupe South discovery consists of two different structures and the oils are produced from the Farewell Formation. Kupe South-2 and Kupe South-3 oil accumulations are situated in the northern part of the structure and are medium brown, waxy oils.

The Toru-1 well lies about half way between the Kupe South discovery and the Taranaki coastline. The light to medium brown, waxy oil flowed from a DST[1] between 3771 m and 3783 m.

*** Stratford discovery**

SAMPLES: Stratford-1

The main production zone of the light yellow Stratford-1 oil lies between 4118 m and 4137 m in the McKee Formation, although other good gas and gas/condensate shows were recorded in several stratigraphic levels in the Kapuni Group.

*** Moturoa Field**

SAMPLES: Moturoa-1, Republic-1, Republic-4, Taranaki-5

The Moturoa-1 oil was discovered in 1866 near New Plymouth. The main oil reservoir lies within sands of the Matemateaonga Formation between 640 m to 701 m. The dark brown oil has an API gravity of 37°, a pour point of 27°C and contains 0.14% S and 39% wax.

The two oils from the Republic wells have API gravities of 33 to 34%, a pour point of 32°C and contain 0.07% sulphur. The Taranaki-5 oil has an API gravity of 32°, a pour point of 32°C and contains 0.06% sulphur and about 30% wax. All oils are produced from very shallow reservoirs.

*** Kora discovery**

SAMPLES: Kora-1 DST2, Kora-1 DST3

The Kora structure is 10 km to 12 km in diameter and is situated in the North Taranaki Graben. The oil reservoir rocks are volcanoclastic sediments and volcanic rocks of Miocene age. Biomarker studies suggest a partial marine source for the oil. The oil is less waxy than oils from other parts of the Taranaki basin and seems to have a lower pour point.

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[1] drillstem test

* Other oil samples from the Taranaki Basin

SAMPLES: Urenui-1, Pukearuhe-1, Waihapa-1

The oil from the Urenui-1 well has a pour point of -1°C and an API gravity of 48°. It is produced from the Mahoenui Formation.

The Waihapa Field is located on the eastern margin of the Taranaki Basin and the oil is produced from fractures in the Tikorangi Limestone (Late Oligocene Age).

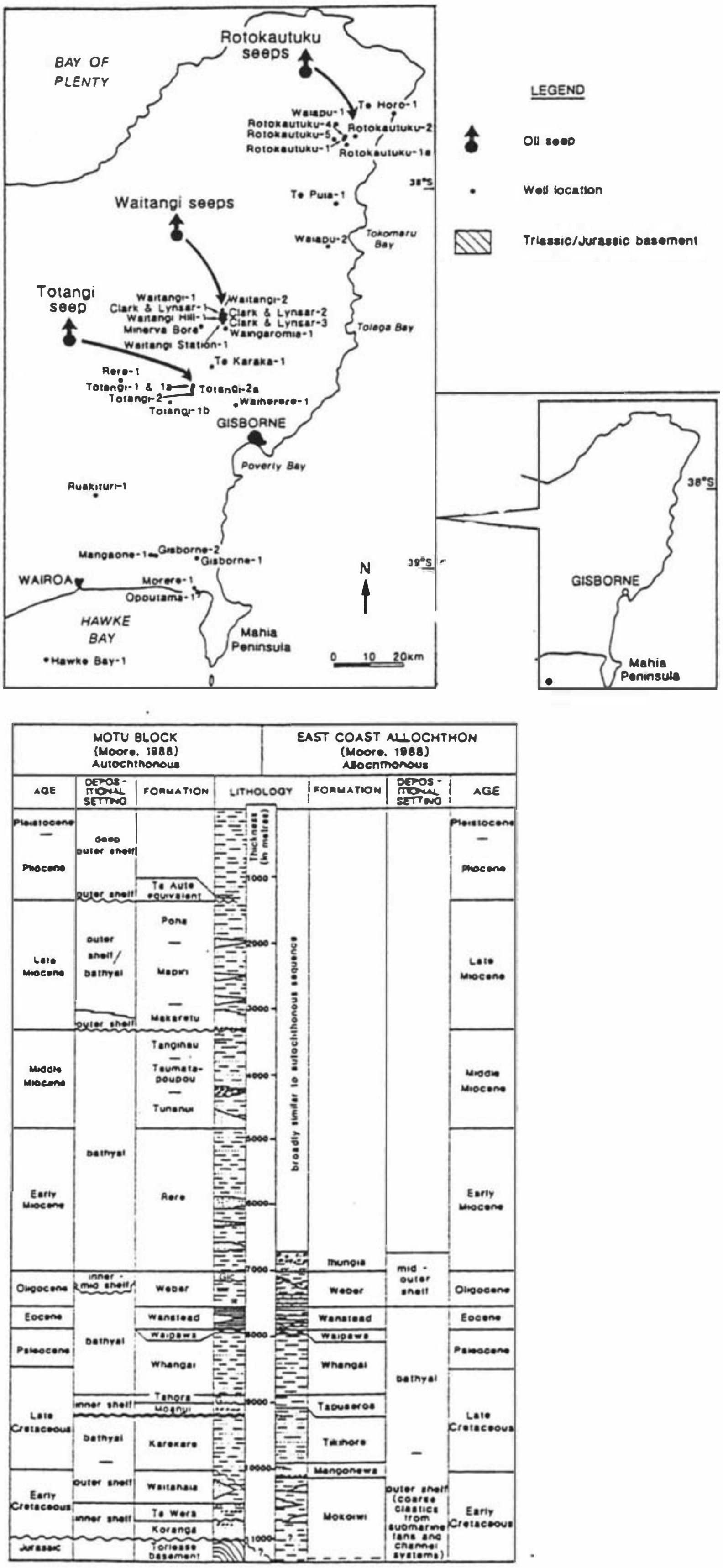
B.East Coast

SAMPLES: Waitangi Seep, Rotokautu Seep

Hydrocarbon occurrences on the East Coast of New Zealand include various oil seeps and widespread oil impregnation of rocks. Figure 7 shows an outline of the basin with locations of hydrocarbon occurrences and stratigraphy.

Source rocks for oils are of marine origin with a possible minor terrestrial influence although no positive identification and oil-source rock correlation has yet been achieved. The Waipawa Black Shale is seen as potential source rock and it has a high content of organic material containing Type II and Type III kerogen (*Geosearch 1991, Ministry of Commerce 1992)*. Although samples analysed are immature, it is believed that the shale could have obtained thermal maturity for hydrocarbon generation at greater burial depths (*Geosearch 1991, Ministry of Commerce 1992)*. The Waitangi and Rotokautu oils have been collected on site and show contamination from high amounts of soil, plant and animal matter. The Waitangi and Rotokautu seep oils contain 0.4% and 0.12% sulphur respectively.

Figure 7: East Coast hydrocarbon occurrences and stratigraphic map (after Ministry of Commerce 1992)

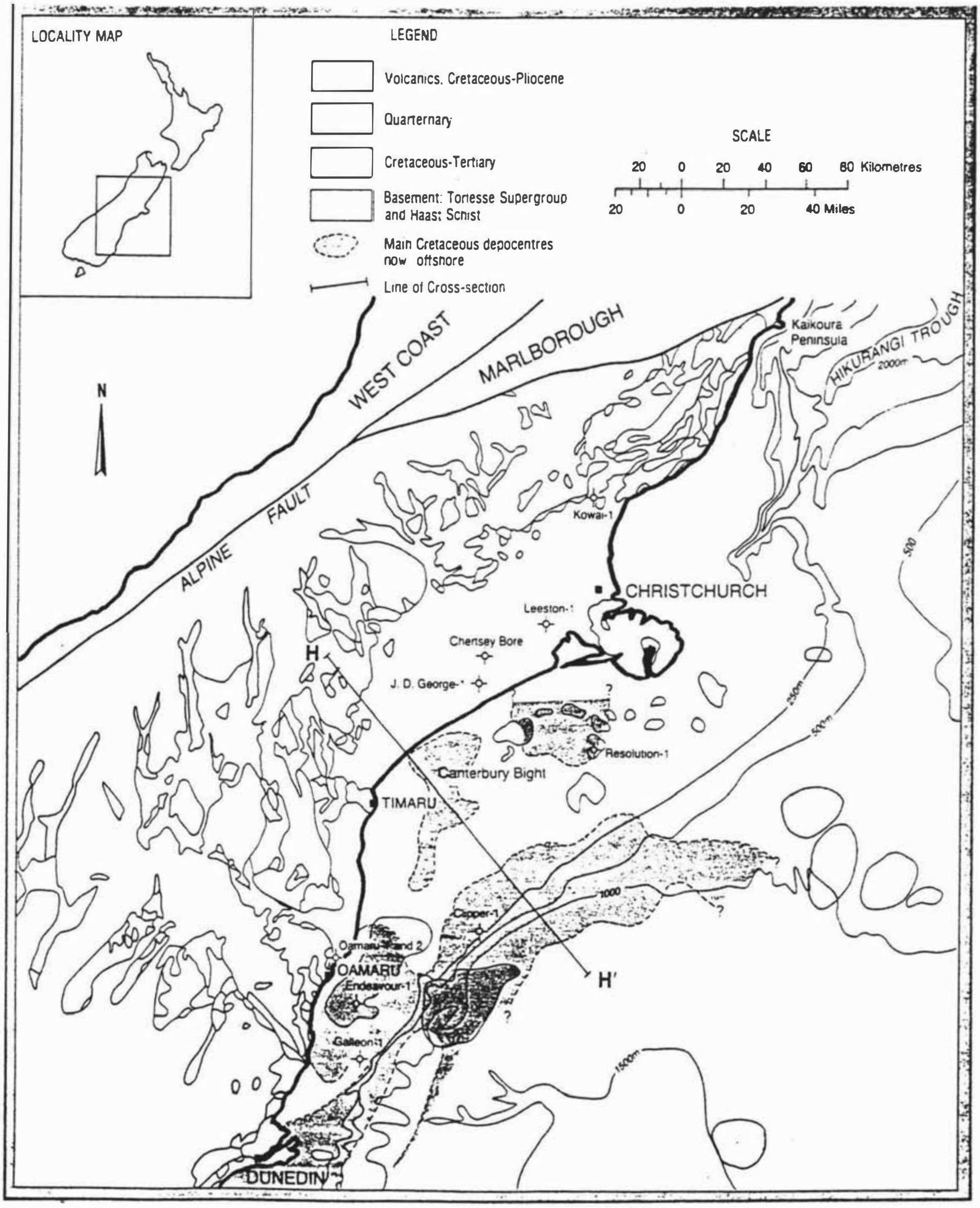


C. Canterbury Basin

SAMPLES: Galleon-1 condensate

The Galleon-1 well in the Canterbury Basin has produced a colourless liquid condensate from an estuarine sandstone interval of Cretaceous age. Figure 8 shows the location and geology of the Canterbury Basin.

Figure 8: Hydrocarbon occurrences in the Canterbury Basin (after Geosearch 1991)



D. Westland Basin oils

SAMPLES: Kotuku seep oil, Blackwater-1 condensate

Source rocks in the Westland Basin are probably the Late Cretaceous Paparoa and Brunner coal measures. They are only mature enough to produce oils in localised areas, especially along major fault lines in the area. Figure 9 shows the area and hydrocarbon occurrences, Figure 9a and 9b depict the stratigraphic maps of the Westland and Murchison Basin. The Kotuku seep oil is dark brown in colour, has an API gravity of 29°, a pour point of -2°C and contains 1.2% wax and 0.16% sulphur.

The Blackwater-1 condensate originates in the Murchison Basin and probable source rocks are carbonaceous units in the Late Eocene Maruia Group and Late Miocene Longford Formation. The condensate contains 0.01% sulphur and has an API gravity of 50°.

Figure 9: Hydrocarbon occurrences in the Westland and Murchison Basin, South Island, New Zealand (after Geosearch 1991)

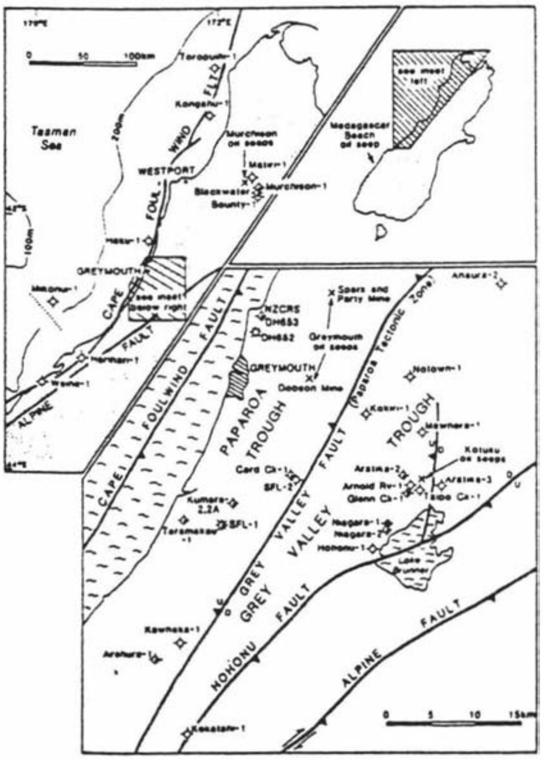


Figure 9a: Stratigraphic column of the central (Greymouth) Westland Basin (after Geosearch 1991)

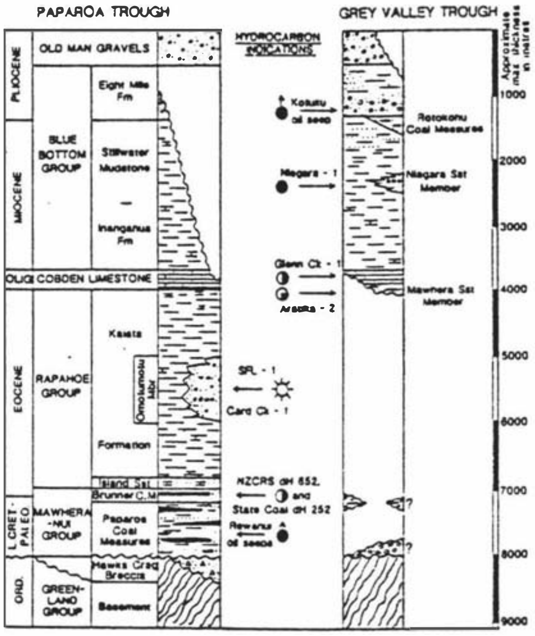
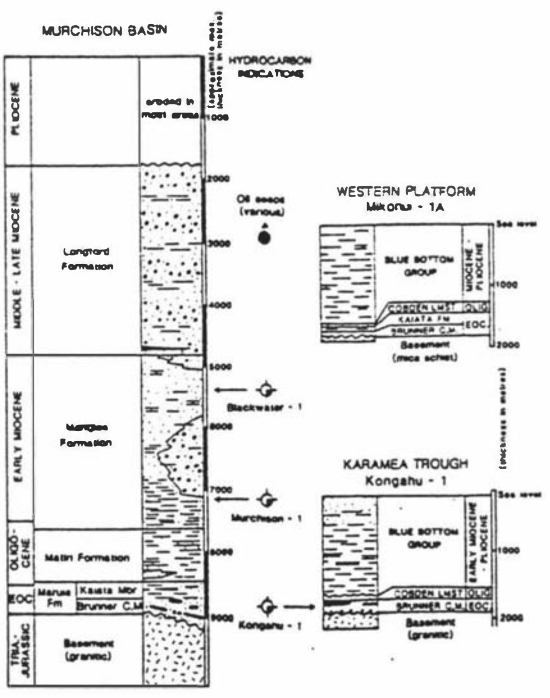


Figure 9b: Stratigraphic column of the Murchison Basin (after Geosearch 1991)



2.3. Overseas Oils

2.3.1 China

*** Jiuxi Basin: Qingxi and Shibei Depression**

SAMPLES: 5 oil samples from Yaerxia oilfield (#114, #502, #503, #506, #507)
1 oil samples from Laojunmiao oilfield(#194), Yumen oil sand, oil sample from
Baiyanghe oil field (#68)

Figure 10 gives an overview of the region. The source rock in the Qingxi and Shibei depressions are late Jurassic to Early Cretaceous black lacustrine shale. Oils from the Yaerxia, Laojunmiao and Shiyougou Oilfields formed at about 4000 m depth and have migrated up to 30 km from west to east. The Yumen oil sand represents the furthest migrated hydrocarbon sample of this system. The oil produced in the Baiyanghe Oil field is derived locally (*Wang* and *Coward 1993, Luo, pers. comm.).*

*** Minhe Basin, Gansu Province**

SAMPLES: Hutouya oil, Minhe Bridge oil sand

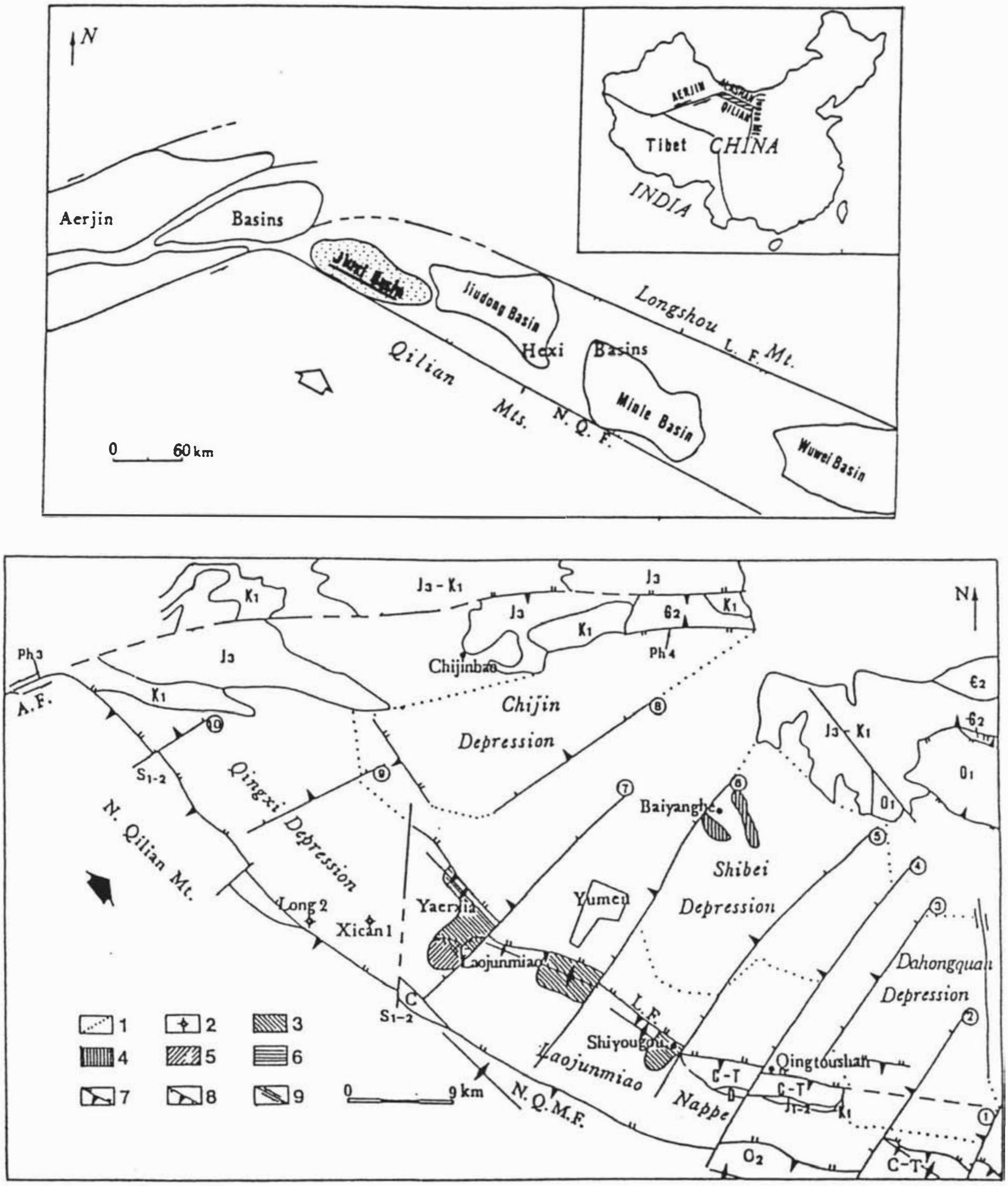
The oil is probably derived from non-marine Jurassic coal seams or interbedded oil shales (*Collen, pers. comm.).* The oil impregnated in the sandstone probably originates from the same source.

*** Turpan Basin, NW China**

SAMPLES: Toucan-1 (Yilahu Oilfield), Qiketai seep oil
Taican-1 (Shanshan Oilfield)

The oil from the Toucan-1 well is probably generated by an Upper Permian freshwater lacustrine sediment with a high input from terrestrial plant matter. The Qiketai oil seeps from Jurassic sandstones and has the same source as the Toucan-1 oil. The source of the Taican-1 oil is Lower to Middle Jurassic coal measures (*Collen, pers. comm.).*

Figure 10: Hydrocarbon occurrences and structural map of the Juixi Basin, China (after Wang and Coward 1993)



2.3.2. Australia

*** Cooper/ Eromanga Basin**

SAMPLES: Alwyn-1, Bagundi-1, Big Lake-37, Brumby-2, Dullingari-29, Dullingari-29, Gidgealpa-16, Gidgealpa-17, Gidgealpa-20, Kidman-5, Lepena-1, Meranji-1, Merrimelia-6, Merrimelia-12, Spencer-3, Strzelecki-5, Strzelecki-10, Taloola-1, Tantanna-1, Wancoocha-2

The Cooper Basin is located in South Australia and the southwest corner of Queensland. An overview of oil well location and stratigraphy is given in Figures 11 and 11a. Hydrocarbons have been generated from Permian and, locally, Jurassic coal measures or land plant-rich sequences. The Permian source rock is classified as Type III kerogen and is rich in inertinite and vitrinite, whereas the Jurassic source rocks are of vitrinite-rich mixed Type II/Type III kerogen (*Kantsler et al. 1984*). Hydrocarbon accumulations have been found in Permian, Triassic and Jurassic reservoirs (Figure 11a).

All oils from the Cooper/Eromanga Basin are light (39° to 56° API) with pour points of around 40°C and have a low sulphur and high wax content. The Merrimelia oils come from a Triassic reservoir, are of Permian origin and are water-washed. Geochemical studies suggest that the hydrocarbons in Jurassic reservoirs are of a bacterially enriched, mixed Type II/Type III kerogen source. Oils found in the Murta Member are geochemically different due to a minor marine influence in the source rock.

*** Timor Sea**

SAMPLES: Challis-7

The oil from the Challis-7 well has probably a marine source (*Collen, pers. comm.*).

Figure 11: Hydrocarbon ocurrences in the Cooper/Eromanga Basin, Australia (after Kantsler et al. 1984)

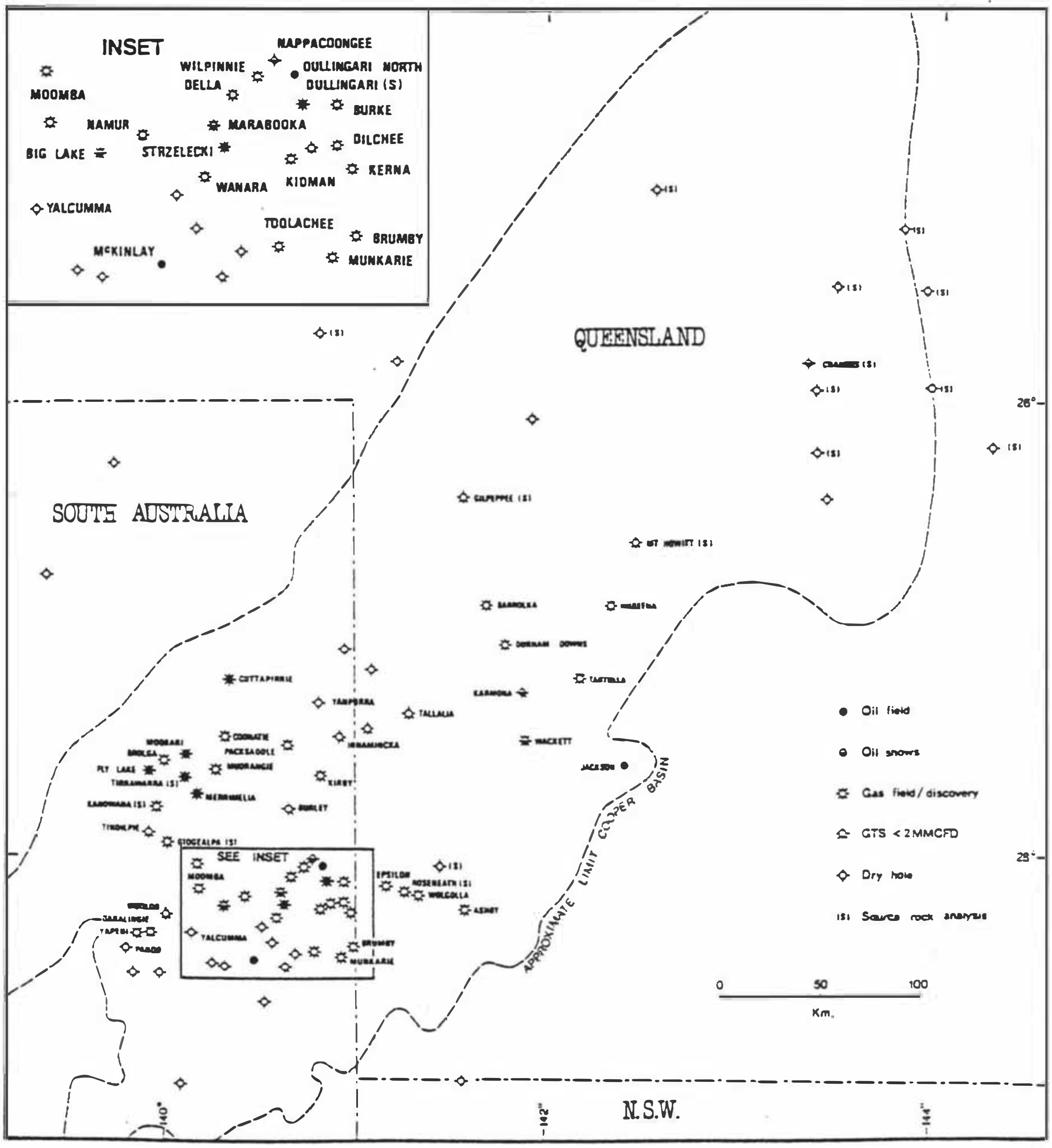
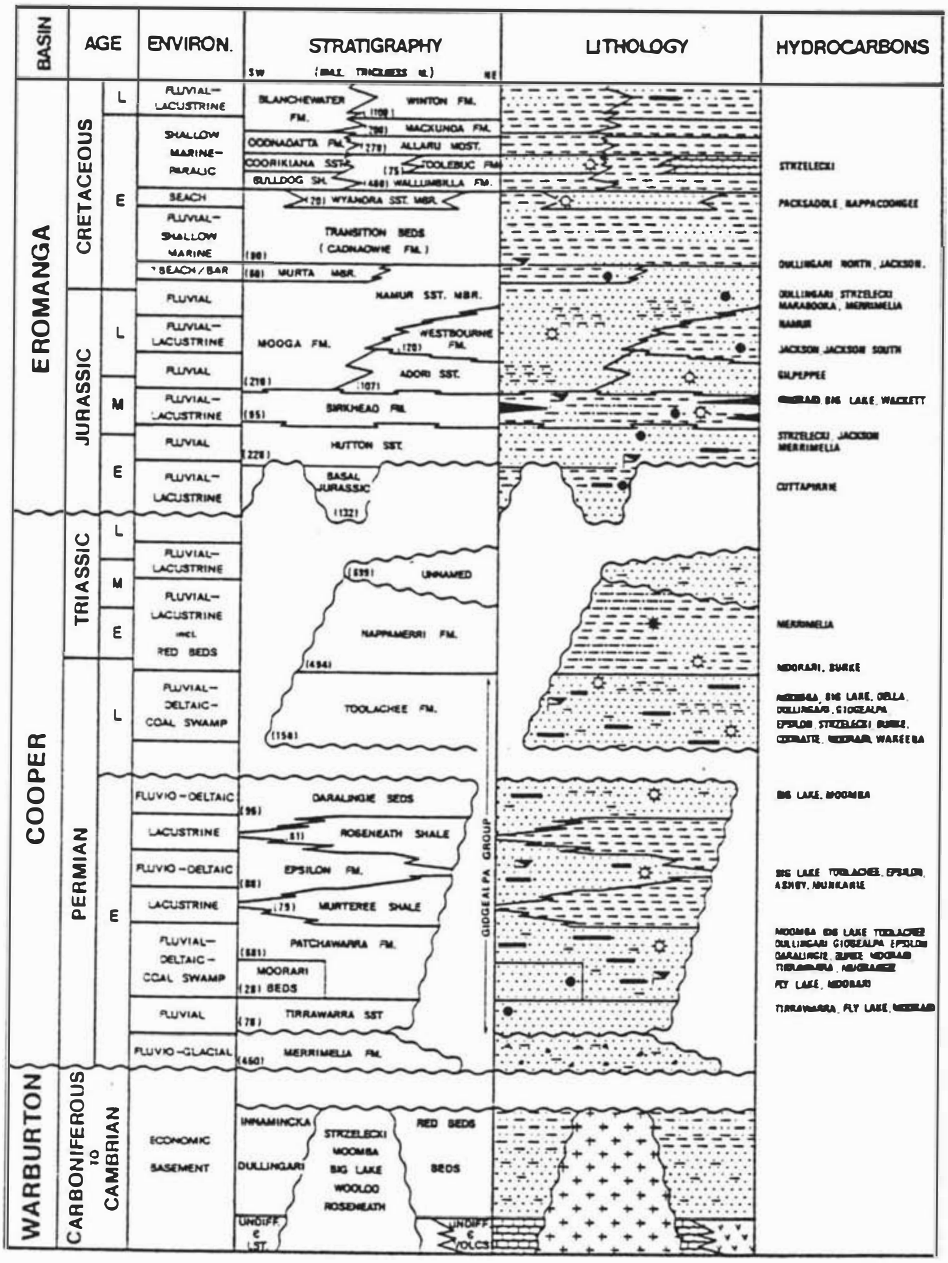


Figure 11a: Stratigraphic column of the Cooper/Eromanga Basin, Australia (after Kantsler et al. 1984)



2.3.3. USA

*** San Juan Basin - New Mexico and Colorado**

SAMPLES: Florence-6A, Florence-7A, Mansfield-1A

The oils were formed from Upper Cretaceous coal beds in the Fruitland Formation which contains predominantly vitrinite and small amounts of liptinite (*Clayton et al. 1991*).

*** Los Angeles Basin oils**

SAMPLES: Hondo-3, Hondo-5, Hondo-7, Hondo-7, Hondo-9, Hondo-12, Hondo-22, Hondo-23, Hondo-24, Hondo-29, Hondo-33, Hondo-37

The oils of the Los Angeles Basin have been generated from Miocene marine source rocks deposited under anoxic conditions. Hydrocarbon accumulations are found in the Miocene age Monterey Formation. The oils are relatively heavy with API gravities between 15° and 19.5° (*Exxon 1992*).

*** Williston Basin - Montana**

SAMPLES: R.P.Oliver-4 (Ivanhoe Dome Field, Musselshell County), Texas-1B (Big Wall Field, Musselshell County), Continental-1 (Sumatra Field, Rosebud County), McAlester Fuel Co-5 (Sumatra Field, Rosebud County)

The source rocks for the Williston Basin oils are interbedded black mudstone, shale and limestone units with secondary beds of dolomite, gypsum and coal of Mississippian age. They were deposited in a coastal swamp to marine environment. Hydrocarbons accumulated in Early Pennsylvanian sandstones, except for the Texas-1B oil which has a carbonate reservoir rock. The API gravities lie between 16° and 36° (*Exxon 1992*).

*** Uinta Basin**

SAMPLES: Alfreda Knudsen-1 (Uinta County), Carter-1 (Flat Mesa Field, Duchesne County), Orlan Johnson-1 (Walker Hollow Field, Uinta County)

The Uinta Basin oils were generated from lacustrine source rocks deposited in the Eocene Green River Formation. The organic matter is type I/ type III kerogen and contains lacustrine algae, bacteria and terrestrial higher plants. The reservoir age is Early to Middle Eocene. The average sulphur content lies between 0.06 and 0.17% (*Exxon 1992).*

*** Gulf of Mexico**

SAMPLES: Humble-3 (Yazoo County, Mississippi), Clark oil Co. (Clarke County, Southern Alabama)

Potential source rocks are the Late Jurassic calcareous Smackover Formation and the Late Cretaceous Tuscaloosa Formation, which is a siliciclastic shale dominated by organic matter derived from terrestrial higher plants. The API gravities for the Clark and Humble-3 oils are 13° and 27° respectively (*Exxon 1992).*

*** Alaska**

SAMPLES: Prudhoe Bay

Geochemical studies suggest that the Prudhoe Bay oil may have up to three different sources - Cretaceous, Jurassic and Triassic marine shale (*North 1985).*

2.3.4. North Sea

*** Norwegian oils**

SAMPLES: 25/11-1 (Balder oil Field), 25/8-1 (Balder oil Field), 3 oil samples from the North Sea - OMC 4755, OMC 3168, OMC 5217 (Kimmeridge Shale source rock)

The Balder Field oils are sourced by a siliciclastic shale deposited under marine anoxic conditions in the Late Jurassic. They have an API gravity of about 21° and contain about 0.7% sulphur (*Exxon 1992, Cooper* and *Barnard 1984, Goff 1984*). The other three oils are of low, medium and high maturity and were generated from the marine Kimmeridge Shale of Jurassic age.

2.3.5. Canada

*** Alberta Basin**

SAMPLES: Husky Mobil Rainbow, Imperial Legal

The oil from the Husky Mobil Rainbow well has a marine calcareous mudstone with carbonate units as its source. The marine algal and bacterial organic matter was deposited in the Middle Devonian. A marine siliciclastic shale of Late Cretaceous age generated the Imperial Legal oil from a Type II kerogen (*Exxon 1992*).

2.3.6. Middle East

SAMPLES: 3 Middle East oils generated from a marine carbonate source rock, Saudi Arabian light oil

The three Middle East oils have the carbonate Huqf Formation as their source and have low, medium and high thermal maturity.

The Saudi Arabian light oil is a mixture of crude oils from the Abquaiq, Abu, Hadriya, Damman, Fadhili and Ghawar fields. The oil has an API gravity of 33.5°, a pour point of -34°C and contains 1.76% sulphur and 1.2% asphaltenes.

2.3.7. Nigeria

SAMPLES: OMC 3813 (terrestrial source), OMC 78 (marine source)

Samples from Nigeria have two different source rocks. One oil is derived from organic matter and the other from a marine source rock.

2.4 SOURCE ROCKS

2.4.1 NEW ZEALAND

Rock samples from 5 different oil wells in the Taranaki Basin were studied to determine trace element concentrations and possible oil/source rock correlations. The samples were collected as washed well cuttings from the Core Store of the Institute of Nuclear and Geological Sciences. The coal fractions used for analytical work were handpicked from the mixed samples. A complete list of samples and sample depths is given in Table 2.3. Samples chosen from the Maui-4, Cook-1, North Tasman-1 and Fresne-1 wells are from sections within the Pakawau Group which is regarded as the most likely source rock for Taranaki oils. The samples from the Toko-1 well are from coal fractions of the Kapuni and Farewell formations.

Table 2.3: Well samples

WELL	SAMPLE DEPTHS [m]
Toko-1 A	4759-4777
Toko-1 B	4456-4474
Toko-1 C	4180-4192
Maui-4	3655-3667
North Tasman	2527-2551
Cook-1	2262-2280
Fresne-1	2501-2502

The terrestrial Pakawau Formation is exposed in the north-west Nelson region (South Island) and samples from four different coal exposures were included in this study. Trace element concentrations of Wairoa, Puponga, North Cape and Mangarakau coals were determined to establish possible correlations to Taranaki hydrocarbons. Samples were collected by J.D. Collen.

Two samples of the Waipawa Black Shale (Taurekaitai Stream and Otoro Stream, Hawkes Bay) from the East coast of New Zealand were also studied.

2.4.2 OVERSEAS SAMPLES

Rock samples considered to be the likely source of the Yumen oils (Jiuxi Basin, China) and samples of the Pritchard Bitumen and Pritchard Bitumen/Carbonaceous Shale from the San Juan Basin (Fruitland Formation) were obtained for trace element studies.

2.5 FORMATION WATER SAMPLES

Seven formation water samples from Taranaki Basin wells (Kupe South-1, Tuhua-1, Pukemai-2B, McKee-1, Pukearuhe, Kupe South-4, Kaimiro-1) were analysed for their trace element concentrations.

III. ANALYTICAL METHODS AND SAMPLE TREATMENT

Trace elements in the oil samples were determined by various analytical methods. Instrumental neutron activation analysis (INAA) and graphite furnace atomic absorption spectrometry (GFAAS) were found to be the best analytical methods for the analysis of crude oils, as oils could be analysed without any significant pretreatment and a wide range of trace elements could be determined.

Problems were encountered in the determination of elements by GFAAS. This was caused by the low element concentrations in New Zealand oils and the complex organic sample matrix. Ashing and acid-oxidations are techniques commonly used to destroy organic matrices. Various attempts to destroy the organic matrix of crude oils, such as dry ashing at high temperatures or oxidation of the samples with mineral acids, were not successful, as they resulted in loss of trace elements.

Undiluted and untreated oils were used for the determination of trace elements by INAA. The dilution of samples with toluene and the use of a mixed solvent system allowed the quantification of several elements by GFAAS and good agreement between the two analytical methods was achieved.

3.1 SAMPLE TREATMENTS

3.1.1. REAGENTS AND EQUIPMENT

A. Reagents and Equipment

All solvents and acids used in the preparation of sample and standard solutions were analytical-grade reagents. Twice-distilled n-heptane was used for the precipitation of asphaltenes.

TLC high purity grade Merck silica gel without binder was used for preparing 2 mm-thick preparative thin layer chromatography (TLC) plates. Pre-coated Merck chromatography plates (2 mm thick) were also used in some TLC experiments.

Whatman ashless filter paper #542 was used in all filtrations of oil and aqueous solutions.

B. Glassware

Only glass flasks and bottles were used for the preparation and storage of oil samples and standards. A waxy organic residue could be found in most glassware after usage which could not be readily removed by hot water and detergent. The dirty equipment was soaked in a mixture of KOH and isopropanol (100 g of KOH dissolved in 50 mL of water, diluted to 1 L with isopropanol) which acts as a degreasing agent and removes traces of wax and organic residue.

If this treatment was not effective enough, the dirty equipment was soaked for several minutes in a 1:1 mixture of fuming HNO_3 and concentrated H_2SO_4, which chars all organic residue. Flasks, beakers and pipettes used in the preparation of standard and sample solutions were soaked overnight in aqua regia to remove contamination by trace elements adhering to the glass. After pretreatment, all glassware was washed and thoroughly rinsed with de-ionised water.

Polypropylene beakers used in the HF/HNO_3 treatment of rock and coal ash were soaked in aqua regia for several hours, cleaned with detergent and rinsed with de-ionised water.

3.1.2 OIL SAMPLES

A. Filtering

Three New Zealand oils (Pukemai-2B, Waihapa-1, Maui-1) showed visible signs of contamination (soil) and were filtered before trace element analysis. Most Taranaki oils have a relatively high pour point and are solid at room temperatures of about 20°C. Oils were filtered in a drying oven at temperatures of 35-40°C to keep them liquid.

To study the effect of filtration on the trace element content of New Zealand oils and hopefully gain some information about the nature of trace element complexes, samples of Toe Toe-2B oils were filtered through Whatman filter paper and a millipore filter. If most of the trace elements are bound to complexes in the soluble heavy oil fractions such as resins and asphaltenes, filtration should not have a major effect. If finely dispersed minerals are responsible for part of the trace element content, this should be reflected in the trace element concentrations as at least part of the mineral grains will have been removed by filtration.

A known amount of Toe Toe-2B oil was diluted with toluene and the resulting oil solution was divided into three equal parts. One part was filtered through a Whatman # 542 filter paper, the second part was filtered through a 0.2 micron millipore filter, and the third part was left untreated. After filtration, the solvent was allowed to evaporate in a fume hood, samples were reweighed and then analysed by INAA. Concentrations of major trace elements for the untreated and filtered Toe Toe-2B oil are shown in Table 3.1.

Most elements (e.g. Br, Cl, Co, and Ni) were not affected by the filtration and variations in concentration lie within the error of the NAA analysis. The higher values for Zn and Cr after filtration with filter paper might be due to contamination by either the filter paper or, more likely, glassware. Only Na and As values are lower after filtration through the 0.2 micron millipore filter. The trace elements in the Toe Toe-2B oil appear to be bound to the organic molecules in the oil and a contribution by minerals is not apparently significant.

Table 3.1: Trace element concentrations in filtered and unfiltered Toe Toe-2B oil solutions

	Toe Toe-2B unfiltered toluene sln.	**Toe Toe-2B** filtered	**Toe Toe-2B** filtered, Millipore
Al (µg/g)	< 8.15	16.6	13.0
As (ng/g)	19.6	20.9	10.4
Br (ng/g)	162.7	141.1	194.4
Cl (µg/g)	21.2	27.0	21.2
Co (ng/g)	16.5	19.8	15.1
Cr (ng/g)	71.3	219.0	96.5
Fe (µg/g)	2.6	6.8	n.d.
Mn (ng/g)	34.0	101.9	60.3
Na (µg/g)	9.1	8.2	3.2
Ni (µg/g)	0.7	0.4	0.5
Zn (µg/g)	0.4	2.3	0.9

B. Ashing

The trace element analysis of oils in organic solvents and especially the determination of V by GFAAS (discussed in part 3.4.5 and 3.1.2, part G) is associated with many problems due to the complex organic matrix of oil samples. The analysis of aqueous sample solutions offers several advantages. The oils could additionally be analysed by ICP-ES, the organic matter interfering in the analysis by GFAAS would be removed, aqueous standards could be used, and trace elements of particular interest could be separated by solvent extraction to concentrate them and minimize possible interferences from other elements.

The high temperature ashing of organic matter is a common, easy and effective technique to remove the organic matrix of oils and obtain a residue soluble in dilute acids. However, the loss of volatile elements and complexes, e.g. volatile Ni and V porphyrins (*Hofstader et al. 1976)* can be a problem.

About 3 g of Tuhua-2 oil was weighed into a glass boiling tube and heated in a muffle furnace to 550°C. About 5 mL of solution are needed for ICP analysis and as trace element concentrations in New Zealand oils are very low, a minimum of three grams of sample had to be used to ensure detectable trace element concentrations in the final solution.

The oil ignited at a temperature of about 250°C and was burnt until all organic matter had been ashed. During burning, a large amount of soot was deposited over the inside of the muffle furnace. The resulting ash in the container and on the inside of the furnace was readily oxidised at 550°C in about 90 minutes and no residual organic or mineral matter was visible in the glass tube. After cooling, about 3 mL of dilute HCl was added and the glass boiling tube was covered with a watch glass. The liquid was lightly heated and allowed to reflux to remove all soluble matter from the side walls of the tube. The solution was then transferred to a flask and diluted to 5 mL with dilute HCl. The results of the analysis by ICP are shown in Table 3.2.

The burning of the oil caused ash to be deposited inside the furnace, resulting in loss of material and, probably, trace elements. A second experiment using the same amount of oil was performed, heating the oil in stages, to try to prevent the ignition of the sample. First, the sample was placed in a drying oven for 12 hours at temperatures of 100°-110°C to evaporate all highly volatile organic compounds. The residue was then slowly heated in stages in the muffle furnace. The temperature was raised every half hour by 50°C until the final temperature of 550°C was reached. The sample still ignited at about 250°C with soot being deposited inside the furnace. No further analysis of this sample was undertaken.

A comparison of major trace element concentrations obtained by NAA and dry-ashing/ICP shows partial loss of many trace elements during ashing and only Co and Ni values agree closely, although other studies showed that Ni is frequently lost during ashing (*Hofstader et al. 1976*). The dry ashing of oils was considered to be an unreliable method as significant losses of trace elements could be observed.

Another method frequently used in the destruction of the organic matrix of crude oils is wet-ashing with concentrated sulphuric acid followed by ashing of the obtained coke in a muffle furnace (*Fabec* and *Ruschak 1985*, *Forteza* and *March 1984*).

A Stratford-1 oil sample (about 1.6 g) was weighed into a porcelain dish and mixed with the same amount of concentrated H_2SO_4. The mixture was heated under stirring on a hotplate until most of the sulphuric acid had evaporated and a black coke-like substance was left. The sample was then ashed at 550°C in 2 hours. No residue was visible and the dish was rinsed with 2 mL dilute HCl and the acid solution analysed for Ni by GFAAS. Nickel was chosen for analysis as its concentration in dry-ashed oil agrees closely with values in untreated oil obtained by NAA indicating that it is obviously not lost during the ashing process. Nickel is moreover one of the most important trace elements in oils and Ni in aqueous solutions is readily determined by GFAAS. Theoretically, the Ni content of the solution was 0.3 µg/mL (calculated from the Ni value obtained by NAA). The analysis by GFAAS showed no measurable amounts of Ni even after 10 multiple loadings. *Fabec* and *Ruschak (1985)* observed in their wet-ashing experiments that the presence of red Fe_2O_3 and silicates prevented the complete dissolution of Ni and V. They treated their samples with HF to remove the silicates and were able to obtain good Ni and V results after this treatment.

A second sample (5 g) was treated exactly as described above to examine the possibility that Ni is lost through incomplete dissolution. After addition of HCl, the solution was transferred to a polypropylene beaker and taken to dryness. Hydrofluoric acid (2 mL) was now added and the sample was heated to dryness over a water bath. The beaker was rinsed with 5 mL of dilute HCl and the solution analysed for Ni by GFAAS. No signal was obtained, even after multiple loadings, and the procedure was not pursued further. As Ni in New Zealand oils is present in extremely low concentrations, it is probably lost through adsorption to the porcelain dish and the polypropylene beaker.

Both ashing methods readily destroyed the organic material, but showed poor trace element recoveries for many elements probably due to volatility and adsorption. Only Co and Ni values in the dry-ashed samples, showed good agreement with the concentration values obtained by NAA. Dry ashing could be used as a decomposition technique if only these elements are to be studied, but it was not considered to be suitable for the study of a wide range of trace elements.

The low temperature ashing (LTA) of one oil sample was undertaken at the Department of Geology, University of Canterbury, Christchurch. After several days, a tough, varnish-like residue was obtained which could not be oxidised further. As this procedure needed a large amount of oxygen, was very time-consuming and as the LTA instrument was only available at another university, no further LTA ashing experiments were undertaken.

C. Acid Oxidation

Organic matter can also be oxidised by a variety of acids and acid mixtures (*Gorsuch 1970)* and the resulting residue is soluble in dilute acids and can easily be analysed by GFAAS and ICP. Temperatures involved in acid oxidation are considerably lower than with dry or wet-ashing methods and the risk of losing volatile elements is greatly reduced. As the samples are not taken to dryness, the loss through adsorption to the container should be minimal.

One of the most effective oxidising reagents is a 4:1 mixture of concentrated HNO_3 and $HClO_4$. Nitric acid breaks organic molecules into smaller fragments which then are easily decomposed by perchloric acid. The addition of concentrated sulphuric acid to a mixture of nitric and perchloric acids increases the oxidising power of this mixture by dehydrating the $HClO_4$. The reagent mixture can effectively decompose even difficult organic samples. Additionally, H_2SO_4 prevents the uncontrolled concentration increase of $HClO_4$ occurring after the evaporation of nitric acid and it helps to avoid explosions caused by violent reactions of perchloric acid with unoxidised organic compounds (*Gorsuch 1970, Martinic* and *Schilt 1976).*

A sample of Tuhua-2 oil (0.5 g) was weighed into a glass boiling tube and 4 mL of concentrated nitric acid was added. The sample reacted violently with the mixture giving off brown NO_2 gas. The sample was slowly heated for 10 minutes in a heating block and as soon as the violent reaction ceased, 1 mL of perchloric acid was slowly added to the clear, dark red liquid. The heating was controlled very carefully to avoid the boiling over of the liquid and to slow down the evaporation of the acids. After most of the nitric acid had evaporated, the sample was allowed to cool. A further 5 mL of acid mixture was added as large amounts of unoxidised matter were still present. This last step was repeated twice until the sample was completely oxidised. A total volume of 20 mL of acid mixture was necessary for complete decomposition.

The solution turned a pale yellow colour after about 90 minutes and the liquid was evaporated to about 1 mL. The cooled sample was then transferred to a flask and diluted with de-ionised water to 5 mL. The sample was analysed by ICP-ES and results are shown in Table 3.2.

Larger amounts of oil (1.0 g to 1.5 g) required substantial amounts of acids (up to 50 mL) and several hours reaction time were needed for complete oxidation of the organic material. The use of large volumes of acids increased the risk of contamination from the reagents. It was necessary to partly oxidise the oil with nitric acid before adding perchloric acid as otherwise an explosion of the sample could not be avoided.

A second sample of Tuhua-2 oil (1 g) was weighed into a glass boiling tube and 0.5 mL of concentrated H_2SO_4 was added. The volume of sulphuric acid was kept as low as possible. Strongly acidic solutions cause problems in the trace element determination by GFAAS and ICP and the high temperature required for evaporation of excess H_2SO_4 (boiling point 338°C) increases the risk of losing volatile compounds. The sample was heated until charring was visible, then 5 mL of fuming nitric acid was added and, after subsidence of the violent reaction, the sample was heated for 10 minutes. Perchloric acid (5 mL) was added and the sample reduced to about half its original volume. It was necessary to add another 7 mL of $HNO_3/HClO_4$ (1:1) mixture, as a light yellow, waxy organic residue was still visible in the solution. After a further 30 min, the clear solution was evaporated to about 1 mL and diluted with de-ionised water to 5 mL. The results of the trace element analysis by ICP are listed in Table 3.2.

The decomposition of crude oils in open vessels had several disadvantages. The rapid evaporation of acids involved the use of large amounts of reagents, thus increasing contamination, and highly volatile compounds could still be lost. The relatively uncontrolled increase of $HClO_4$ in oxidation experiments without H_2SO_4, frequently resulted in loss of sample due to explosive reactions of the perchloric acid with organic compounds. The oxidation under reflux seemed a good alternative as it would keep the acids in longer contact with the sample, hopefully decreasing the amount of reagents required and minimizing the risk of loss of very volatile compounds. *Walker et al. (1976)* treated crude oils with a mixture of $H_2SO_4/HNO_3/HClO_4$ under reflux and were able to determine selenium in the resulting solutions. In previous experiments, Se was partially lost during acid oxidation in an open vessel, which was attributed to the presence of nitric acid in the mixtures and the degree of charring of the samples. The addition of HNO_3 under reflux prevented the loss of Se by volatilization.

A 1 g sample of Tuhua-2 oil was weighed into a 50 mL glass flask, 0.5 mL of sulphuric acid was added and a water-cooled condenser was connected to the flask. The sample was heated on a hot plate for 10 minutes until charring was visible. After cooling, 5 mL of fuming HNO_3 was added and the dark red liquid was refluxed for about one hour. After cooling, 5 mL of perchloric acid were added dropwise through the condenser while stirring the solution. The sample was then heated slowly to about 150°C. If the heating was not monitored closely, and was performed quickly, uncontrollable violent foaming occurred resulting in loss of sample. After about two hours of heating, a waxy, light yellow coloured substance (sulphur) was still floating on top of the liquid. A further 10 mL of acid mixture was added and the sample was refluxed for another hour. The condenser was then rinsed with de-ionised water, allowed to drain and the solution was taken down to about 2 mL. After cooling, the yellow liquid was transferred to a volumetric flask and diluted to 5 mL with de-ionised water.

The same procedure was repeated with a second sample of Tuhua-2 oil to test reproducibility of the procedure. Results of trace element analyses by ICP-ES of both solutions are shown in Table 3.2.

A minimum of three hours was necessary to achieve complete oxidation of the oil. Although the acids remained in longer contact with the solution, the volume of reagents required for total decomposition was about the same as the volume used in the open vessel oxidation. The sample solution becomes increasingly diluted as water is formed during the oxidation reactions which is not evaporated under reflux. Fuming nitric acid was chosen to keep the water content of added acids as low as possible.

To gain some information about the volatility of trace elements, acid oxidation was carried out on an aqueous solution (BEC 1) containing several trace elements in different concentrations. This solution is used as a standard in the trace element determination by ICP-ES. A quantity of the standard solution (5 mL) was evaporated to near dryness and the experiments were carried out using exactly the same procedures and amounts of reagents as described above. Trace element concentrations in the original and acid-treated solutions are listed in Table 3.3.

The results can only give an indication of the behaviour of trace element compounds under these conditions, as the metal compounds in crude oil probably react quite differently from trace elements in the form of dissolved inorganics in an aqueous solution. As the trace element concentrations of some elements in the standard are 10 to 100 times higher than in New Zealand crude oils, contamination by acids and loss of volatile compounds will have a lesser effect on the overall results of the analysis of the standard solution.

A blank solution was also analysed to check trace element contamination introduced by the acids. A total of 20.5 mL of H_2SO_4, HNO_3 and $HClO_4$ (ratios as described above) were boiled in a boiling tube, and the liquid was evaporated to about 1 mL and diluted again to 5 mL with de-ionised water. Trace element values for the blank solution are shown in Table 3.2.

Trace element concentrations varied greatly between the different oxidation procedures. Iron seemed to be lost, possibly due to incomplete dissolution or adsorption. The main contaminant, Na, that was probably introduced by the acids as the blank value, has a very high concentration.

Table 3.2: Trace element concentrations (µg/g) in untreated, ashed and acid-oxidised Tuhua-2 oil

	Tuhua-2 untreated	**Tuhua-2** ashed	**Tuhua-2** $H_2SO_4/HNO_3/HClO_4$ reflux	**Tuhua-2** $H_2SO_4/HNO_3/$ HClO4 reflux, repeat	**Tuhua-2** H_2SO_4/HNO_3 $/HClO_4$ boiling tube	**Tuhua-2** $HNO_3/HClO_4$ boiling tube	**Blank**
Al	13.70	2.11	1.41	166.32	6.00	24.23	1.60
Co	0.01	0.01	*n.d.	*n.d.	*n.d.	*n.d.	0.02
Cr	0.17	0.06	*n.d.	*n.d.	*n.d.	*n.d.	0.09
Cu		0.08	1.85	0.88	1.93	0.70	0.15
Fe	7.08	1.54	3.41	3.30	5.31	4.07	2.8
Mn	0.08	0.04	0.47	*n.d.	0.05	*n.d.	0.05
Na	11.30	8.28	46.47	58.20	69.75	80.85	12.6
Ni	0.20	0.27	1.75	0.77	0.88	2.42	0.19
Pb		0.27	9.45	*n.d.	8.72	*n.d.	2.9
Zn		0.21	4.13	2.00	3.02	2.01	0.56

* = trace element concentration below detection limit in the original solution

Table 3.3: Trace element concentrations (in µg/g) in aqueous standard BEC 1, before and after acid treatment

	BEC 1 original concentrations	**BEC 1** $HNO_3/HClO_4$ boiling tube	**BEC 1** $H_2SO_4/HNO_3/$ $HClO_4$ boiling tube	**BEC 1** $H_2SO_4/HNO_3/$ $HClO_4$ reflux	**BEC 1** $H_2SO_4/HNO_3/$ $HClO_4$ reflux
Al	32.0	67.5	161.3	27	46.9
Co	2.0	1.6	1.5	1.7	2.3
Cr	2.0	1.5	1.6	1.5	0.9
Cu	5.0	4.5	4.5	4.7	6.0
Fe	5.0	4.8	4.7	4.7	7.7
Mn	1.0	0.8	0.8	0.9	1.2
Na	90.0	82.8	98.5	93.7	111.9
Ni	5.0	4.3	3.9	4.2	5.9
Pb	20.0	1.4	1.5	1.8	23.4
Zn	2.0	1.9	1.8	1.97	2.8

Another possibility is the leaching of Na and other trace elements from the glass container which is subjected to strong acids, high temperatures and long reaction times. The main problem was the poor reproducibility of the experiments involving oxidation under reflux. Results varied considerably although both experiments were carried out using the same reagents under the same conditions. The concentrations of some trace elements in the blank solution were equal to or higher than the concentration of trace elements in oil.

The results for the BEC 1 standard agree reasonably well with the original concentrations and high losses of volatile compounds or adsorption effects could not be observed. Only the Pb content was affected strongly and this element is probably lost as $PbSO_4$ in the oxidation experiments using H_2SO_4, where it may precipitate in the presence of $CaSO_4$ (*Temminghoff* and *Novozamsky 1992).*

The BEC 1 samples are less affected by contamination introduced by acids, as trace element concentrations are 10 to 100 times higher than element levels in New Zealand oils.

The oxidation of New Zealand oils with acids is not a very satisfactory procedure, mainly due to the length of reaction time needed for complete decomposition and the large volumes of reagents required. The trace element content of the analytical-grade acids is nevertheless high enough to contaminate the sample solution considerably and the reproducibility is unsatisfactory.

Other strong oxidising reagents are Br_2 and H_2O_2. Their effectiveness in decomposing crude oils was tested in combination with nitric acid or nitric/sulphuric acid mixtures. The oxidations using Br_2 were not complete even if large volumes of reagent were used. The oxidations with mixtures of H_2O_2/HNO_3 and $H_2SO_4/HNO_3/H_2O_2$ required large volumes of hydrogen peroxide as H_2O_2 is only available in 30% solution. The main problem with the use of hydrogen peroxide was the occurrence of violent foaming when the sample solution was only slightly heated. Most of the sample was lost during this stage and it was not possible to completely oxidise the oil even with large amounts of reagent and very careful heating.

The use of a closed vessel (Teflon bomb) prevents the loss of elements and high temperatures can be achieved due to the increased pressure in the bomb. A Tuhua-2 oil sample was heated with concentrated nitric acid and perchloric acid (4:1 mixture) in a tightly closed Teflon bomb. However, the pressure build-up was too high and the bomb exploded. The decomposition of oil in a small closed Teflon bomb in a microwave oven has the advantage of being less time consuming, but only very small samples (about 0.1 g) can be used and the procedure required relatively large volumes of acid. None of the above-mentioned procedures was satisfactory and they were not pursued any further.

D. Extractions

The very low trace element concentrations in New Zealand oils and interferences from the complex oil matrix caused many problems in the determination of Ni and V by GFAAS. Liquid-liquid extraction is a technique used for the separation of one or several trace elements of particular interest from a sample matrix and the metals can be concentrated in small volumes of the extracting reagent. Usually, elements are extracted from aqueous solutions into a suitable organic solvent or complexing reagent. This was not a viable option for the separation of trace elements from crude oils as organic solvents are soluble in petroleum. No literature is available about the extraction of metals from oils into an aqueous phase or other reagent. *Hofstader et al. (1976)* tested extractions of trace elements from crude oils. They extracted arsenic with silica gel or Raney nickel. All extractions were incomplete and the procedure was limited to a small range of elements.

In many crude oils, V and Ni exist as porphyrin complexes with V^{4+} and Ni^{2+}, but not much is known about the nature of non-porphyrinic complexes of V and Ni and the complexes of other trace elements in crude oils. Oxidising V to V^{5+} might help to break the V-porphyrin bond and strong acids might destroy complexes releasing the trace elements. Several aqueous reagents were tested for their effectiveness by extracting the Venezuelan standard oil. The aqueous phase was analysed for Ni and V by GFAAS. The standard oil was chosen as it contains high concentrations of V and Ni, easy to detect by GFAAS.

The oil was extracted with several acids, using oxidising and/or complexing agents. About 5 mL of undiluted oil and oil/toluene mixture were shaken with 2 mL of H_2O, HNO_3 (2M, 6M, concentrated), HCl (2M, 6M, 11.4M), 6M HNO_3/2% H_2O_2, dilute HCl/$KMnO_4$, H_2SO_4 (2M and 18M), aqua regia (3:1 mixture of conc. HCl and HNO_3), concentrated HBr, dilute HCl/APDC (ammonium pyrrolidine dithiocarbamate). After shaking, the mixture was centrifuged to separate the two phases and then allowed to stand for several minutes.

All concentrated acids were miscible in the oil and could not be recovered fully as the phases did not separate. Concentrated nitric acid, sulphuric acid and the hydrogen peroxide mixtures partly oxidised the oil. The oxidised particles were visible as a black precipitate. The dilute acids were only very slightly soluble in the oil, but none of the above reagents extracted a high percentage of Ni and V from the crude oil. The best result - about 20% recovery of Ni - was obtained with a mixture of 2M H_2SO_4/H_2O_2.

Extractions with the same reagents were carried out on a Tuhua-2 oil sample and the resulting aqueous phase was analysed for Co, Fe, Ni and V by GFAAS. No measurable amounts of any of these elements could be detected and no further extraction experiments were undertaken.

E. Solvents

Most New Zealand oils are solid at room temperature due to their high pour point and wax content and had to be diluted with a suitable organic solvent prior to trace element analysis by GFAAS. Only the condensates could be analysed without dilution as they are already liquid and therefore easy to inject into the graphite furnace. Their trace element content is extremely low and further dilution would have lowered trace element concentrations in the samples below the detection limit.

A commonly used solvent in trace element analysis by atomic absorption spectrometry and ICP-ES is xylene. Other organic solvents used in trace element studies include methyl-isobutyl ketone (MIBK), tetrahydrofuran (THF) and toluene (*Fabec* and *Ruschak 1985, Brodie* and *Matousek 1971, Šebor et al. 1975, Bruhn* and *Cabalín 1983).*

The New Zealand oils did not completely dissolve in MIBK, even when diluted 25 times. Both toluene and xylene dissolved the oils completely, although slight heating to 35-40°C was necessary for some high wax samples to dissolve completely. Toluene was used in all experiments as it was readily available as very pure analytical grade reagent. A 2:1 ratio of solvent to oil was ideal, as samples dissolved completely and the trace element concentrations in the resulting solutions were still above the detection limit.

Marine oils with higher trace element concentrations were diluted 10 times (about 1 g oil in 10 mL toluene). Standard stock solutions in toluene, prepared with NBS fuel oil and Venezuelan crude oil, were diluted as required for trace element analysis.

F. Mixed solvent system

Accurate results for trace element analysis of crude oils by GFAAS can only be obtained if the matrix of the standard solution matches the sample matrix very closely. Oil standards with certified trace element values are available but most standards contain only a very limited number of certified trace elements and are expensive. Organic metal complexes dissolved in solvents have also been used as standards in flame atomic absorption spectrometry, but they are not readily available. The solution matrix does not match the sample matrix and metal complexes are quite different to the complex mix of trace metal compounds in crude oils.

Several studies investigated the use of mixed solvent systems by which a small amount of oil can be rendered compatible with an aqueous inorganic salt solution to avoid the cost and problems associated with the available standards.

Holding and *Matthews (1972)* and *Holding* and *Noar (1970)* used lubricating oils and aqueous standards dissolved in toluene/isopropanol (9:1) and cyclohexanone, butanol, methanol (5:3:2) mixtures to measure Ca, Zn, Ba and Mg concentrations by flame AAS. Aqueous solutions (10 mL) or up to 300 mg of oils were soluble in 100 mL of the mixtures. *Osibanjo et al. (1984)* used a toluene/acetic acid mixture (ratio 1:4) to determine the Ni, Cu, Zn, Na, Pb, Cd and Fe contents in Nigerian crude oils. The oils were not soluble in acetic acid but this reagent was used to improve the burning characteristics of the solutions in the flame. Other solvent mixtures were tested but formed emulsions with the oils. The trace element concentrations were in the µg/mL range and the coefficients of variation were around 10%.

Mixtures of toluene/acetic acid, toluene/isopropanol, toluene/methanol and toluene/isopropanol/acetic acid in varying ratios were tested for their ability to dissolve New Zealand crude oils. Only toluene/isopropanol dissolved the oil samples completely. A 3:7 ratio of toluene to isopropanol was found to be effective in dissolving oils and aqueous solutions equally well. Oils formed emulsions with mixtures containing acetic acid and methanol. The analysis of one emulsion showed low, incorrect Ni concentrations. It is crucial to dissolve the oil first in toluene before adding isopropanol, to avoid precipitation of the oil. Up to 10 mL of aqueous inorganic salt standards are soluble in 100 mL of the toluene/isopropanol mixture.

The method was tested for its accuracy and applicability to the trace element analysis by GFAAS. The Ni concentration in solutions of the NBS fuel oil standard, Maui-1, Tariki-1 and Kotuku seep oils in toluene/isopropanol were determined and compared with the Ni values obtained by the NBS for the fuel standard and INAA for the New Zealand oil samples. Nickel standards were prepared from a 1000 µg/mL inorganic Ni-salt standard solution and diluted with toluene/isopropanol to 0.1, 0.2, 0.5 and 1.0 µg/mL.

The solubility of New Zealand oils in the toluene/isopropanol mixture depended on the waxiness of the samples. Between 0.4 g and 0.7 g of oil was soluble in 5 mL of solvent mixture. Very waxy oils tended to precipitate in higher concentrations and had to be diluted by a higher factor. About 0.5 g of oil was weighed into a 5 mL or 10 mL volumetric flask, dissolved in toluene and then the flask was filled with isopropanol. It was necessary to slightly warm some oils to completely dissolve them in toluene before the addition of isopropanol as otherwise oils tended to precipitate. Before analysis, the sample solutions were shaken and lightly heated in warm water to ensure complete dissolution of the oil and even distribution of the phases. The solutions degraded quickly, although it was possible to keep them in the refrigerator overnight. The oils started to precipitate after about 2 days as isopropanol and toluene evaporated.

The Ni concentration in the oil solutions was determined by GFAAS using the absorption line at 232.0 nm, a 0.2 nm slit width and background correction. Details of the heating cycle and analysis are given in chapter 3.4.5. Three different solutions of fuel oil standard in isopropanol/toluene were each analysed twice. The results given are the mean of two determinations. Two different solutions of Maui-1 and Kotuku seep oil and one solution of Tariki-1 oil were analysed. Ni concentrations are listed in Table 3.4. The analysis of a blank solution showed no measurable Ni contamination of the solvents or any background absorption caused by molecular fragments or smoke.

All concentrations agree with the results obtained by other methods and lie within the error margins. The coefficient of variation for the six measured Ni concentrations in the fuel oil standard is 10%.

Table 3.4: Nickel values in standard oil and some New Zealand oils, determined in a mixed-solvent system

	Ni (µg/g) **determined by INAA**	**Ni (µg/g)** **determined by GFAAS using mixed solvent system**
Fuel oil standard	28.00 ± 2.00 (NBS certified value)	23.12, 23.21, 29.23, 26.81, 27.81, 28.96 mean = 26.52
Maui-1	1.47 ± 0.39	1.43, 1.39, 1.20 mean = 1.34
Kotuku Seep oil	1.36 ± 0.36	1.34, 1.25 mean = 1.30
Tariki-1	1.22 ± 0.43	1.07, 1.06 mean = 1.07

The method was applied to the determination of Cu, Cd, Pb and Zn concentrations in New Zealand, Australian and some marine crude oils. These elements are detectable by GFAAS even at extremely low concentrations. Low detection limits are important for the determination of trace elements in mixed solvent systems, as the oils have to be additionally diluted with toluene/isopropanol, thus lowering the original trace element concentrations considerably. Details of the heating program and graphite furnace work are given in chapter 3.4.5 and results are listed in Appendix E. In Table 3.5, Zn concentrations for some marine and New Zealand oils obtained by GFAAS and INAA are listed for comparison. Data from both methods agreed very well for all concentration levels.

The oils were diluted with toluene/isopropanol as described above and analysed by GFAAS. All standards were prepared from 1000 µg/mL aqueous stock solutions (BDH) and diluted as required. Concentrations of 4 ng/mL Zn, 2 ng/mL Cd and 10 ng/mL Cu and Pb were detectable in the mixed solvent solutions. Final concentrations of Cu, Pb and Zn in New Zealand and Australian oils ranged from 10 ng/mL to 1 µg/mL. Some oils such as Kora-1 and Kupe South-3 had values above 1µg/mL. Cd values for all analysed oils were in the ng/mL range.

Table 3.5: Zn concentrations in some New Zealand oils, determined by NAA and GFAAS

	Zn determined by NAA	**Zn** determined by GFAAS
Waitangi Seep	1.55	1.53
Kupe-2	0.76	0.79
Kupe-3	5.37	4.15
Kupe-4	0.33	0.39
Kora-1	11.2	11.6
Toe Toe-2B	0.38	0.44
Middle East oil	31.48	30.92
North Sea oil	0.13	0.10

G. Nickel and vanadium determination

Vanadium and Ni are the two most important trace elements in crude oils. Their concentrations vary with geographical and depositional environment and they have been useful in oil classifications, oil-oil and oil-source rock correlations. Most Ni and V concentrations in New Zealand crude oils lie below the detection limit of INAA and their concentrations could not be determined by this method.

Ni concentrations in New Zealand oils were determined by GFAAS by analysing undiluted condensates and oil samples diluted with toluene (1:2). The use of NBS fuel oil and Venezuelan crude oil as standards led to erroneous results, as Ni values in New Zealand oils determined by GFAAS (calibrated with NBS standards) and concentrations obtained by NAA differed by more than 50%. This can be partly explained by large errors involved in the determination of Ni by INAA, and is probably also due to the different spreading behaviour of the standard solutions in the graphite furnace tube compared to the highly waxy New Zealand oil samples. Both standard oils contain high amounts of nickel and had to be diluted considerably with toluene to obtain a suitable standard curve. The high amount of solvent, the more aromatic matrix of both standard oils and the different metal complexes all contribute to the different behaviour in the graphite tube, leading to low results for New Zealand oils. A greater dilution of the New Zealand samples to match the matrix of the standard solutions would have lowered the Ni concentrations below the detection limit. Figure 12 shows Ni concentration curves obtained by diluted NBS standards and New Zealand oils.

Nickel concentrations in Maui-4, Tariki-1 and Maui-1 oils were determined by INAA and these three oils were used as standards in the Ni analysis of New Zealand oils and values obtained agreed favourably with INAA concentrations (Table 3.6). Nickel concentrations in all New Zealand and Australian oils, which are similar to Taranaki oils, were determined using Maui-1, Tariki-1 and Maui-1 oil solutions as standards.

Figure 12: Nickel standard curves obtained with NBS oil and Maui-1 oil solutions

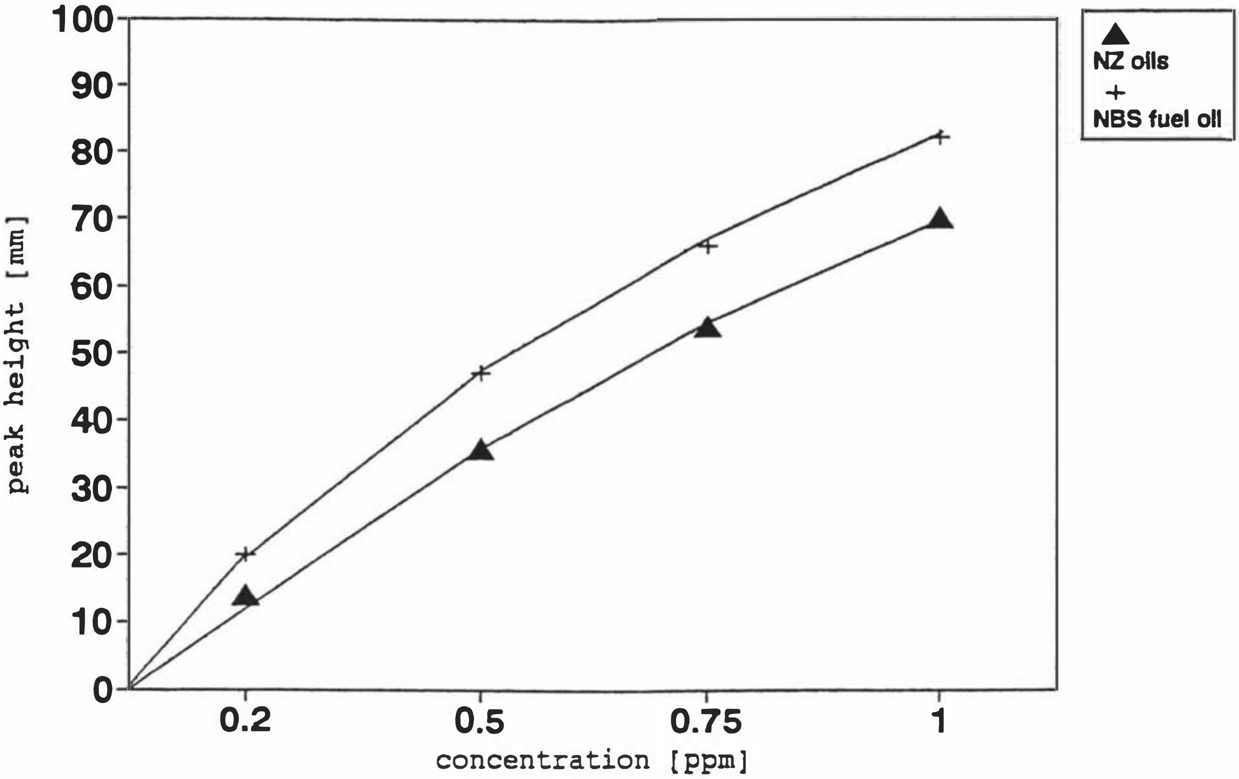


Table 3.6: Nickel concentrations (in µg/g) in New Zealand oils determined by INAA and GFAAS

	INAA	GFAAS				
		fuel oil Std.	Venez. crude oil Std.	Maui-1 Std.	Maui-4 Std.	Tariki-1 Std.
Maui-1	1.47 ± 0.39	0.53	0.83		1.66	1.61
Maui-4	0.91 ± 0.27	0.24	0.24	1.09		0.89
Tariki-1	1.22 ± 0.43	0.35	0.57	1.11	1.26	
Urenui-1	1.50 ± 0.58	0.75	0.94	1.25	1.29	1.15
Moki-1	n.d.[*]	0.34	0.50	1.26	0.82	0.84
McKee-3A	n.d.[*]	0.13	0.36	0.60	0.57	0.56
Toe-Toe-3	n.d.[*]	0.10	0.39	0.73	0.61	0.65
Blackwater Cond.	0.60 ± 0.24	n.a.[**]	n.a.[**]	0.49	0.46	n.a.[**]
Saudi-Arabia	4.00 ±	4.38	4.05	3.71	n.a.[**]	n.a.[**]

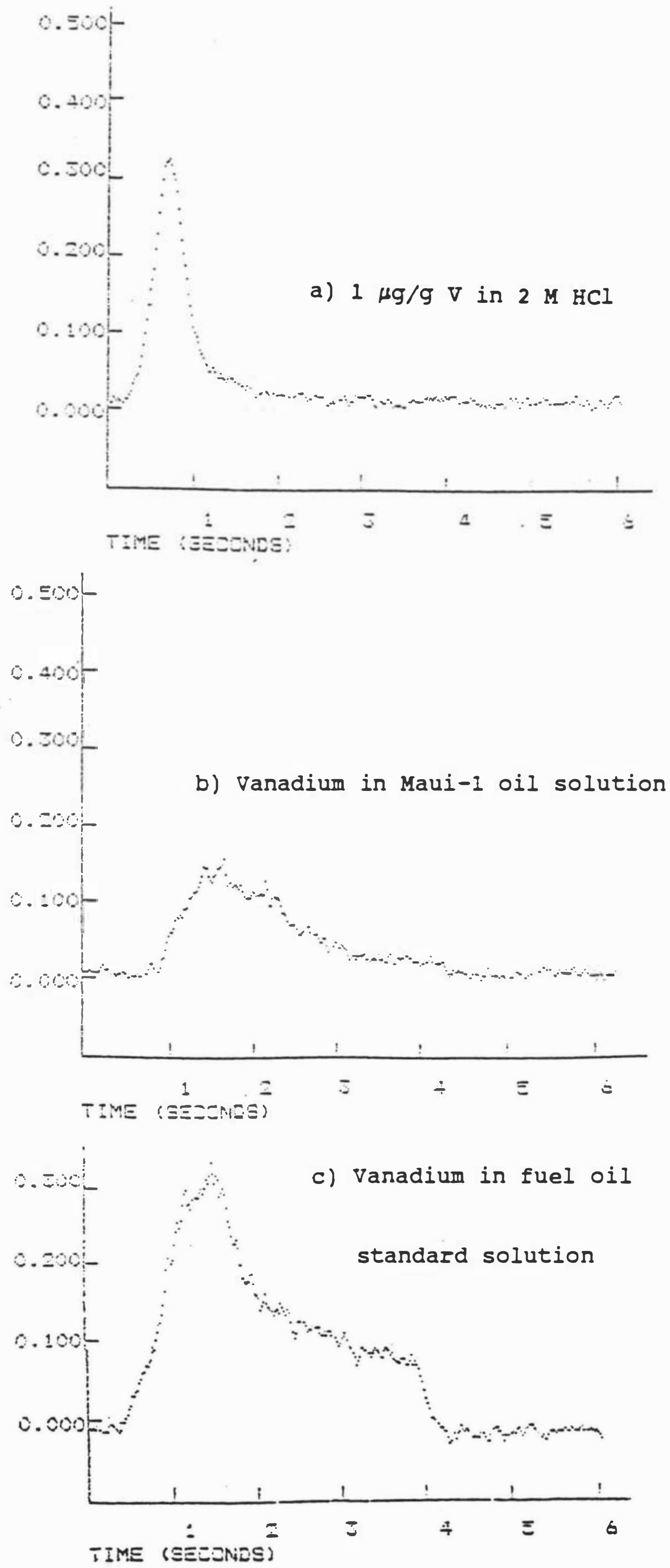
[*] not detected
[**] not analysed

Vanadium is a refractory element and can form stable carbides with other refractory elements and carbon during heating in a graphite tube. The complex behaviour and reactions of V in flame and electrothermal atomic absorption analysis have been studied extensively. The V signal obtained by flame AAS depends strongly on the matrix of the sample and the type of metal bonding in the trace element complex (*Sebor et al. 1975).*

Sebor and *Lang (1977)* added small amounts of halogens (Br_2, Cl_2) to their oil samples to alter the porphyrin complexes and release V, but the V signal was not influenced. The interferences caused by matrix effects and differences in metal-complex bonds should be less pronounced in electrothermal AAS as the organic compounds are ashed before the element is atomized. The ashing temperatures and time have to be chosen carefully to avoid residual organic matter or smoke interfering in the analysis. *Wendl* and *Müller-Vogt (1985)* found in their study that V reacted with carbon, oxygen and other elements during ashing and the resulting compounds interfered in the analysis by GFAAS. The type of V compound formed depended strongly on the ashing time and temperature with oxides and carbides formed at temperatures as low as 500°C (*Wendl* and *Müller-Vogt 1985).* The various oxides and carbides were destroyed at higher temperatures and V was only present as the metal at temperature above 1800°C (*Wendl* and *Müller-Vogt (1985)*, *Manning* and *Slavin (1985))*. No major interferences from other elements or acids were reported by *Barbooti* and *Jasim (1982)* and *Manning* and *Slavin (1985)*, although high amounts of W could lead to the formation of stable mixed carbides. *Manning* and *Slavin (1985)* showed that the formation of carbides, soaking of sample solution into the graphite and subsequent "tailing" were minimised by the use of tube made from pyrolytically coated graphite. They also found that the cooling of the furnace to room temperature between the ashing and atomization step improved the V signals considerably.

Maui-1 and marine oil solutions were analysed by GFAAS at 318.4 nm and calibration absorption peaks of 2 µg/mL V in 2M HCl, V peaks in Maui-1 and marine oil are shown in Figure 13. The signal obtained with the oil solution shows a broader shape with no distinct peak plus tailing due to the slow and delayed release of the element from the graphite tube during atomization. Only about one third of the total V amount was recovered, as the original concentrations had been determined by INAA. Subsequent atomizing resulted in a slow partial release of the absorbed V amount. The recommended cooling down step before the atomization at 2800°C did not improve the signal shape or height. Pre-soaking of the graphite tube with toluene to avoid the absorption of the oil solution by the graphite and the addition of modifiers (conc. HCl, bromine water and $Mg(NO_3)$ as used by other workers (*Sebor* and *Lang 1975*, *Manning* and *Slavin 1985)* did not have any effect on the peak shape or the V amount recovered. Argon was used as inert gas to test if carbides or nitrides are formed during heating, but the signal obtained stayed unaltered. As the oil samples contain high amounts of carbon molecules, carbides could be formed with the carbon of the oil matrix during ashing and this process would not be influenced greatly by the use of argon or pyrolytic graphite. The ashing temperature was varied between 600 and 1900°C and the signal decreased slightly at ashing temperatures above 1100°C without a significant change in the overall shape of the signal. The analysis of a toluene blank after a sample run showed that a significant amount of V was retained on the graphite which was slowly released during subsequent heating.

Figure 13: Peak shapes of V in oil and aqueous solutions



a) 1 µg/g V in 2 M HCl

b) Vanadium in Maui-1 oil solution

c) Vanadium in fuel oil standard solution

The element is not completely removed from the furnace, even at atomizing temperatures of 3000°C. A minimum of three cleaning steps at 3000°C were necessary to remove all residual vanadium from the furnace.

The analysis of V in oil solutions by electrothermal AAS proved to be very difficult due to complex reactions and a pronounced memory effect even if new graphite tubes with intact coating were used. The signal shape and height could not be improved and V concentrations could not be determined in oil samples. Sample runs on the newer GBC system 2000/3000 model resulted in the same problems.

The analysis of V by flame AAS is greatly influenced by matrix effects. The method is also not sensitive enough for the determination of the low V concentrations in New Zealand oils as samples have to be diluted considerably to ensure even sample flow and nebulization into the flame.

The emission line at 437.9 nm has a theoretical detection limit of 0.2 µg/mL (*Ingle* and *Crouch 1988)* and samples of fuel oil and Maui-1 in toluene were analysed by flame emission spectrometry. The fuel oil and Maui-1 sample were diluted with toluene, 25 and 10 times respectively. The background emission of the solvent and oil matrix was very high and any V signals were masked. The rapid build-up of organic residue on the burner presented a major problem. The analysis had to be stopped after only two solutions due to the amount of carbon deposited on the burner head. This would make the analysis of oil samples impossible as not even a standard curve could be obtained before the cleaning of the burner is necessary.

The analysis of V in aqueous solutions by graphite furnace atomic absorption is not prone to serious matrix effects and V in aqueous solutions can be detected down to 0.05 ppm in solution when multiple injections are used (*Frankenberger 1990).* As extraction and wet ashing procedures were not suitable, marine and New Zealand oil samples were dry-ashed in a muffle furnace and dissolved in an acidic solution. Although some V might be lost, the results would still give an indication of the V amounts in oils which were not detectable otherwise.

Marine oil and New Zealand oil samples were weighed into boiling tubes, and the samples were heated to 110°C in a drying oven to evaporate the volatile compounds. Then, the samples were placed in a muffle furnace, heated in stages to 550°C and ashed in about 4 hours. No residual mineral or organic matter was visible in any of the samples. About 3 mL of 2M HCl was added, the containers covered with a watch glass and the acid refluxed for several minutes. After cooling, the solutions were transferred to 5 mL volumetric flasks and filled to the mark.

The samples were analysed by graphite furnace atomic absorption (GBC system 2000/3000). Vanadium standards were prepared in 2 M HCl and a comparison of the V concentration found in NBS Venezuelan oil (286.7 µg/g) with a certified value (390 µg/g ± 10 µg/g) showed that about 25% of the total amount of V was lost during ashing. The V values in fuel oil (56.9 µg/g) and Tuhua-2 oil (0.09 µg/g) agreed very closely with the certified value of the former (55.4 µg/g ± 1.1 µg/g) and INAA result of the latter (0.11 µg/g) with about 18% loss from the Tuhua-2 sample. Losses did not seem to occur for all oils, as the second sample of Tuhua-2 oil and the fuel standard showed values higher than the concentrations obtained by other methods and an increase of all values by 25% seemed not to be justified. Vanadium concentrations are extremely high in Venezuelan oil and the V complexes (porphyrin complexes) in the marine oil are probably very different, with different volatility, to V complexes in New Zealand and fuel oil. Porphyrin complexes can be volatile and could be lost at a greater rate than other V organometallic compounds. Vanadium present in clay minerals would be more stable, explaining the relatively small losses in New Zealand oils. Several marine and New Zealand samples were ashed and analysed, as it was the only analytical method available for the determination of V in oil samples.

Details of the analysis (heating program, RSD and standards) are given in chapter 3.4.5.

3.1.3 OIL FRACTIONS

A. Thin layer chromatography

A high percentage of trace elements is associated with the heavy oil fractions such as asphaltenes and resins. Oils can be separated into aliphatic, aromatic, asphaltene and resin fractions by chromatography (*Tissot* and *Welte 1984*). Column chromatography is a lengthy procedure requiring large amounts of oil and solvents (*Woolhouse, pers. comm.*) and asphaltenes have to be removed before the chromatographic separation as they tend to interfere. Preparative thin layer chromatography offers a good alternative as up to 90 mg of rock extracts, or oil, can be used (*Huc et al. 1976*) and separation can be achieved in a relatively short time without large volumes of solvents. Fractions can be eluted from the gel for further trace element analysis. Chromatography plates 2 mm thick, which are expensive, are used for separations of larger amounts of sample.

A mixture of 75 g silica gel, 7 g of $CaSO_4 \cdot 2H_2O$ and 160 mL water was found to be most suitable as it was easy to spread and dried plates showed the least cracking of all mixtures tested. The glass plates were cleaned with ethanol and the mixture applied evenly with a commercial spreader. Only about two out of ten plates were suitable for TLC experiments, as others cracked considerably during drying.

The oils were dissolved in a mixture of CH_3OH and $CHCl_3$ and applied in a thin, even line. This was achieved with an applicator described by *Bennet* and *Heftmann (1963)*. Two small glass plates were taped together with about 1 mm space between the plates and the two lower edges exactly aligned. The lower end of the applicator was dipped into the oil solution and the liquid was drawn between the two plates by capillary forces. The applicator was then dropped quickly on to the starting line and the liquid flowed on to the silica gel in an even line. The sample was allowed to dry before each additional application of sample.

To separate oil into fractions, *Muirhead (1983)* used cyclohexane and *Martin et al. (1985)* and *Sudbury (1985)* used solvent mixtures. A sample of Tuhua-1 oil was applied to a 2 mm thick TLC plate (Merck silica gel with UV fluorescent indicator) and the plate was placed in a tank lined with chromatography paper and chloroform/methanol mixture (8:2). The plate was removed after the oil had moved about 1/4 of the way up. After drying, the procedure was repeated with the same solvent mixture. To separate aliphatic, aromatic and polar fractions, the plate was run twice with n-hexane. Chromatography plates successively developed with $CHCl_3/CH_3OH/CH_3COOH$/hexane, hexane/toluene and hexane showed equally good separation. The separate fractions were clearly visible under UV light. Oil fractions on TLC plates without the UV fluorescent indicator could be made visible by spraying the gel with a solution of rhodamine B in ethanol.

Oil fractions could be eluted from the gel with methanol or methanol/dichloromethane using several methods. The silica gel containing the fraction was slightly heated with the solvent in a glass container and the solution containing the oil was filtered. Other possible methods are the elution of oil fraction using a miniature-column or the soxhlet extraction of the oil fraction, although extraction and elution in a small column required larger amounts of solvents. The analysis of the eluted aromatic fraction by GFAAS did not show any detectable Ni or Fe concentrations. Usually, between 40% and 90% of trace elements in crude oils are associated with the asphaltene fraction (*Zaki et al. 1989, Fish et al. 1984*) and as trace element concentrations in New Zealand oils are extremely low, concentrations of trace elements in other fractions were well below the detection limit. Trace element studies were then focussed on the asphaltene fractions of New Zealand oils.

B. Asphaltenes

Asphaltenes are defined as the compounds in crude oils not soluble in either n-pentane, n-hexane or n-heptane, but soluble in hot benzene (*Tissot* and *Welte 1984, Miles 1989*). Asphaltenes were separated from New Zealand crude oils according to the Institute of Petroleum standard method for the precipitation of asphaltenes (*IP143/78* and *Muirhead 1983*).

The oils were weighed into a 1 L flask and n-heptane was added (30 mL per one gram of oil). Some 25 to 30 g of New Zealand and Australian oils and 5 to 10 g of marine oils was needed to obtain between 40 and 500 mg of asphaltenes. The oil solution was slightly heated and shaken to ensure complete dissolution of the oil in the solvent. The flask was then left standing overnight and a dark brown precipitate collected on the bottom of the flask. The solution was filtered through Whatman filter paper #542 and the flask was repeatedly rinsed with warm n-heptane to ensure that all asphaltenes were transferred to the filter paper. The filtrate was washed thoroughly with hot n-heptane until the solvent was colourless. Filtration of the waxy New Zealand oils was very slow and took up to two days. The filter paper was covered during longer filtration times to avoid contamination by dust and the lab atmosphere. The filter paper containing the asphaltenes was dried in a drying oven at 100°C for 30 minutes and stored in a desiccator. The asphaltenes were dissolved in toluene using Soxhlet extraction. The filter paper was placed in the Soxhlet extractor and extracted until the solvent returning to the flask was colourless. Toluene was removed by rotary evaporation, the flask dried at 110°C in a drying oven for about 2 hours and then allowed to cool in a desiccator. The flask was reweighed and the amount of precipitated asphaltenes calculated. Asphaltenes from New Zealand, Australian and marine oils were precipitated. A complete list is given in Table 3.7 and asphaltene percentages indicated by an asterisk * are the mean of two separate precipitations. Condensates and very light oils did not contain any measurable amounts of asphaltenes. To ensure comparable conditions for all oils, the samples were usually heated to about 50°C before weighing to remove very volatile chemicals.

Paraffinic oils contain less than 10% resins plus asphaltenes (*Tissot* and *Welte 1984)* and most New Zealand oils contain less than 1% asphaltenes. *Hirner* and *Lyon (1989)* and *Hirner* and *Robinson (1989)* precipitated asphaltenes from New Zealand oils for isotope studies and a comparison of results from this study with values from the two reports agree well for some oils. Table 3.8 compares asphaltene weights obtained in this study with values from the two isotope studies. Variations in results can be explained by the fact that the amount of asphaltenes strongly depends on the type of solvent used. Weighing errors are rather high due to the extremely low amount of asphaltenes and possible loss of asphaltenes during filtration. As the same procedure and reagents were used for all asphaltene precipitations, errors should have been consistent and minimised.

Table 3.7: Asphaltene content of oil samples

Oil	**Asph.** [%]	**Oil**	**Asph.** [%]
Kora-1$^{DST\ 3}$	0.88	Saudi Arabia*	2.86
Kora-1$^{DST\ 2}$	0.36	Venezuela	11.50
Kotuku Seep	0.18	Nigeria,marine	1.38
Kupe-2	0.15	Middle E. 5220	2.29
Kupe-3	0.49	Middle E. 4677*	1.12
Maui-1	0.84	North Sea 3168*	2.38
Maui-4*	0.44	G. of Mexico	4.00
McKee-1	0.48	Williston Basin	10.88
McKee-2	0.28	Hondo-3, USA	4.90
McKee-3A	0.27	Hondo-7, USA	6.00
McKee-4*	0.47	Hondo-24,USA	10.03
Moki-1*	0.80	Prudhoe Bay	10.40
Pouri-1	0.17	Brumby-2*	0.43
Pukearuhe	2.04	Gidgealpa-16	0.94
Pukemai-1B	0.54	Gidgealpa-17	0.30
Republic-1	0.43	Gidgealpa-20^{B}	0.06
Republic-4	0.41	Gidgeapla-20^{TN}	1.02
Stratford-1*	0.19	Merrimelia-6$^{H.}$	0.18
Taranaki-5	0.14	Merrimelia-6$^{N.}$	0.14
Tariki-1A	0.17	Merrimelia-6$^{M.}$	0.29
ToeToe-1	0.08	Merrimelia-12	0.26
ToeToe-2B	0.13	Wancoocha-2	0.09
ToeToe-4	0.16	Yumen 503	1.38
Toru-1	0.35	Yumen 506	1.34
Tuhua-1	0.54		
Tuhua-2	0.12		
Urenui	0.11		
Waihapa	0.36		
Waiotapu	2.53		
Waitangi	1.41		

Table 3.8: Asphaltene content (in %) in New Zealand oils compared with results from other studies

	Asphaltenes (%) **Hirner and Lyon**	**Asphaltenes (%)** **Hirner and Robinson**	**Asphaltenes (%)** **this study**
Waiotapu Seep	1.7	0.8	2.5
Republic-1	1.0	0.4	0.4
McKee-1	1.1	0.6	0.5
Waitangi seep	1.0	2.0	1.4
Republic-4	0.5	0.6	0.4

The asphaltene solutions for GFAAS analysis were prepared in toluene. Asphaltenes were analysed for their Ni, Co, Mn and Fe concentrations using NBS fuel oil and Venezuelan crude oil as standards. Results are listed in Appendix H. As the matrix of the standard solutions matched the asphaltene/toluene solutions relatively closely, results obtained by INAA and GFAAS agreed very closely as is shown in Table 3.9.

Table 3.9: Comparison of Ni and Co concentrations in asphaltenes, determined by INAA and GFAAS

	Ni [µg/g] **INAA**	**Ni [µg/g]** **GFAAS**	**Co [µg/g]** **INAA**	**Co [µg/g]** **GFAAS**
Kora-1	137.8	132.1	10.2	6.2
Maui-1	19.8	18.2	4.2	5.1
Maui-4	35.3	30.2	36.0	21.5
McKee-1	4.9	8.7	0.8	1.2
McKee-3A	5.5	9.0	1.1	1.4
McKee-4	2.0	7.3	1.1	1.1
Moki-1	8.3	10.7	1.0	2.0

The Ni concentrations for McKee-1, McKee-3A and McKee-4 asphaltenes obtained by GFAAS were significantly higher than INAA results. A second analysis of asphaltenes obtained by a separate precipitation procedure gave similar results.

3.1.4 COALS AND SOURCE ROCKS

A. Ashing and HF/HNO_3 treatment

Trace elements in ashed coal and rock samples were analysed by ICP-ES. Samples, except the pre-washed well cuttings, were washed with deionised water to remove outside dirt, dried and finely ground with a mortar or ring mill. The coals from well cuttings were hand picked.

The samples were sieved through a 200 mesh sieve, weighed into a silica crucible and ashed at 550 to 600°C in a muffle furnace. Ashing was usually complete after 6 to 8 hours. Some unoxidised organic matter was still visible after ashing one coal sample at 450°C for three days, but the sample showed the highest trace element recovery. Ashing temperatures of 750°C to 800°C led to high trace element losses (Figure 14).

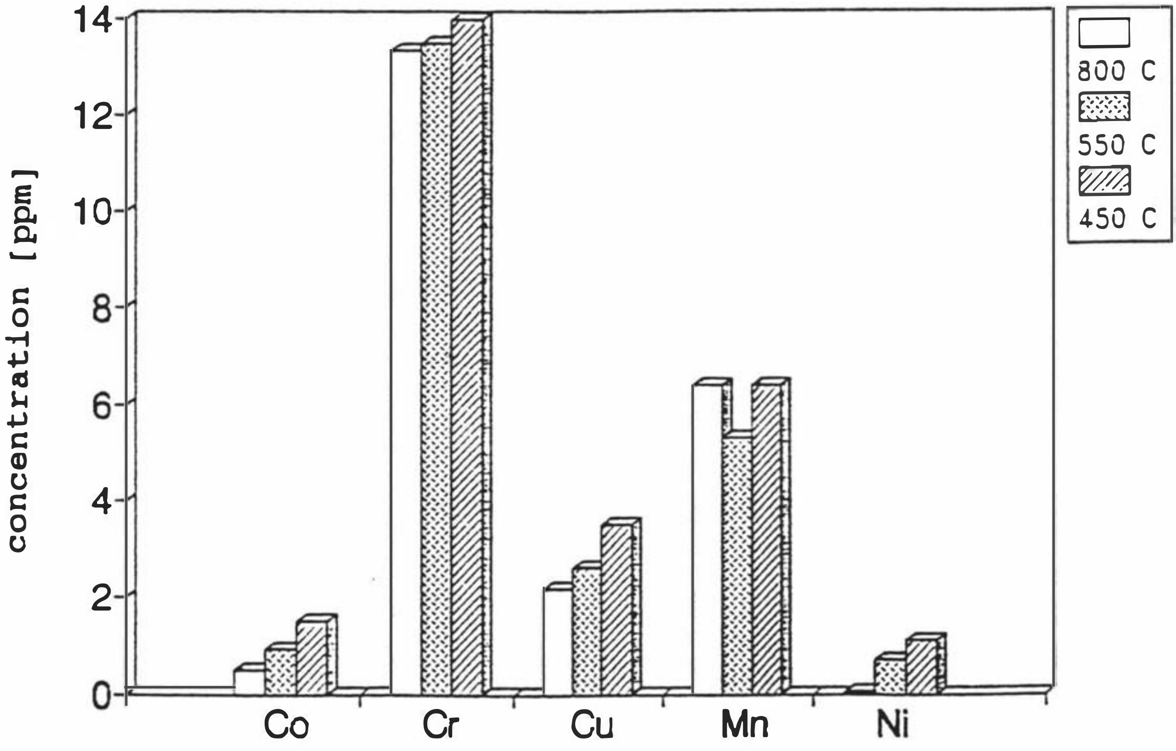
Table 3.10: List coal samples and ash content (in %)

Sample	**Ash [%]**
Mangarakau	91.19
North Cape	94.66
Puponga	77.47
Wairoa	75.63
Toko A	86.95
Toko B	88.95
Maui-4	79.02
Cook-1	64.80
Pritchard Bit.	67.36
Pritchard (carbonaceous shale)	11.90

Samples were ashed at 550°C as all organic matter was oxidised at this temperature. Trace element recovery was good and complete ashing was achieved in several hours. After ashing, the crucible was weighed and the amount of ash calculated. The ash was weighed into a polypropylene beaker and 2 mL of concentrated HNO_3 was added. The sample was heated over a water bath to oxidise any remaining organic matter and after the nitric acid was evaporated, 10 mL of HNO_3/HF (1:1) was added and

the sample was heated to dryness. About 5 mL of 2 M HCl was added and the solution was heated slightly to ensure complete dissolution. The beaker was reweighed to determine the exact amount of HCl added and the solution was analysed by flame AAS to determine its Fe content. Iron concentrations of more than 500 µg/mL would interfere in the ICP analysis and samples were diluted if necessary. Results of the trace element analysis by ICP and V analysis by GFAAS are listed in Appendix G.

Figure 14: Trace element concentrations of coal samples after ashing at different temperatures



B. Bitumen extraction

Bitumen is defined as the organic matter present in sedimentary rocks that is soluble in organic solvents (*Miles 1989*). New Zealand coals and source rocks from overseas samples were extracted with $CHCl_3/CH_3OH$ and analysed for their trace element content to establish possible oil-source rock correlations. Bitumen can be extracted with a variety of solvents such as dichloromethane, benzene/methanol, chloroform, chloroform/methanol (*Durand and Espitalié 1976, Albrecht et al. 1976, Radke et al. 1978, Rice et al. 1989, Jones* and *Philp 1990, Hirner 1987b*). Different solvents result in quite different trace element contents in the final extract (*Filby pers. comm.*) (Figure 15), except Ni and V which showed very constant values with the Ni/V ratio between 0.73 and 0.93.

A sample of Pakawau coal was extracted with different solvent mixtures to investigate extraction yields and trace element recoveries (Figure 16). One coal sample was extracted with $CHCl_3/CH_3OH$ for different lengths of time to determine optimum extraction times and the dried extracts were analysed after removal of the solvent to measure Fe, Ni and Co concentrations (Figure 17). The chloroform/methanol (2:1) mixture was chosen for Soxhlet extractions as it resulted in high extraction yields and good trace element recoveries. The same solvent mixture was also used by *Hirner (1987b)* in a similar trace element study on South German crude oils and source rocks.

The ground and sieved samples were weighed into a Soxhlet cellulose thimble and extracted with a $CHCl_3/CH_3OH$ mixture (2:1) for 72 hours. The extracts were filtered twice through Whatman filter paper #542 and the solvents were removed by rotary evaporation. The dried extracts were analysed by INAA for their trace element contents. Results of trace element analysis are given in Appendix F.

Figure 15: Trace element concentrations in bitumen extracted from shale with toluene, chloroform, toluene/methanol and dichloromethane/toluene (INAA values after *Filby, pers. comm.*)

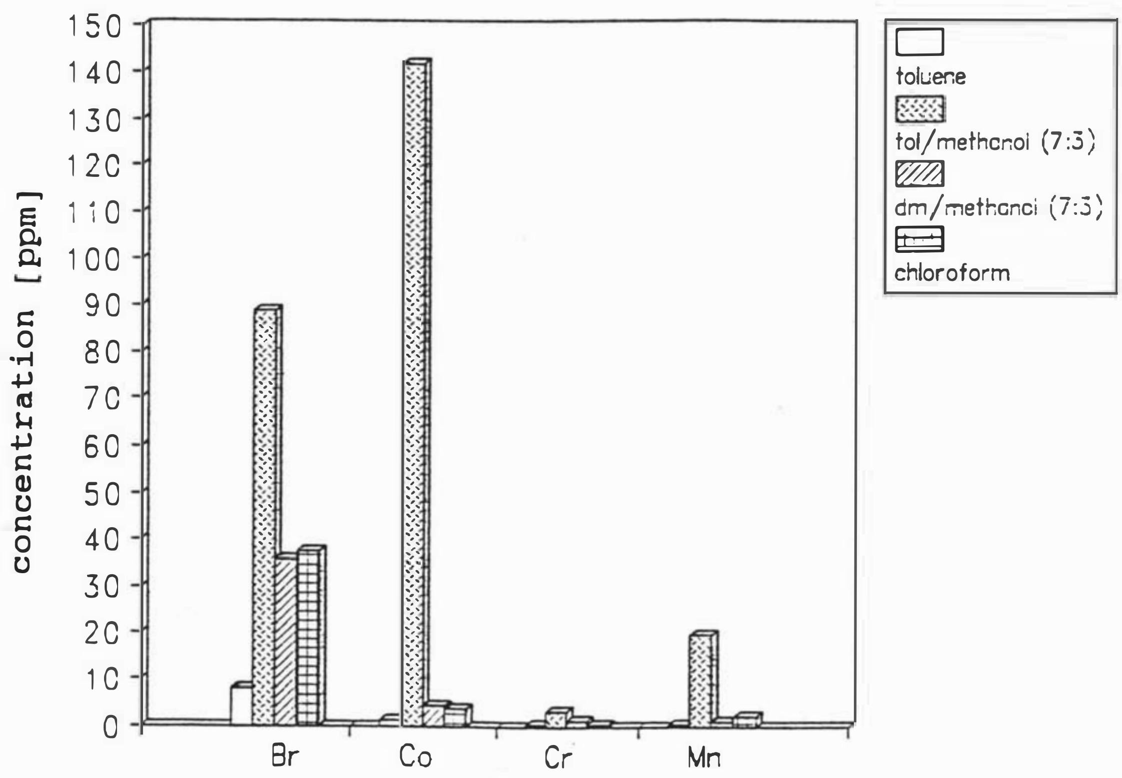


Figure 16: Trace element concentrations bitumen extracted from New Zealand coal with different solvents

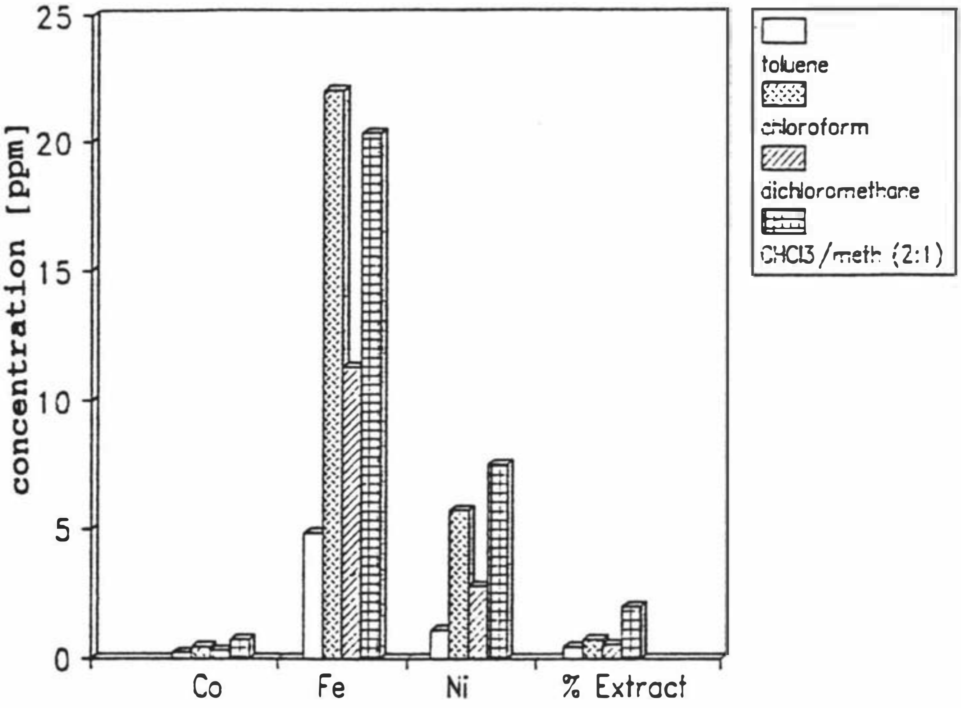


Figure 17: Nickel and Fe concentrations in bitumen obtained after 6,12, 24,48 and 72 hours extraction of coal with chloroform/methanol

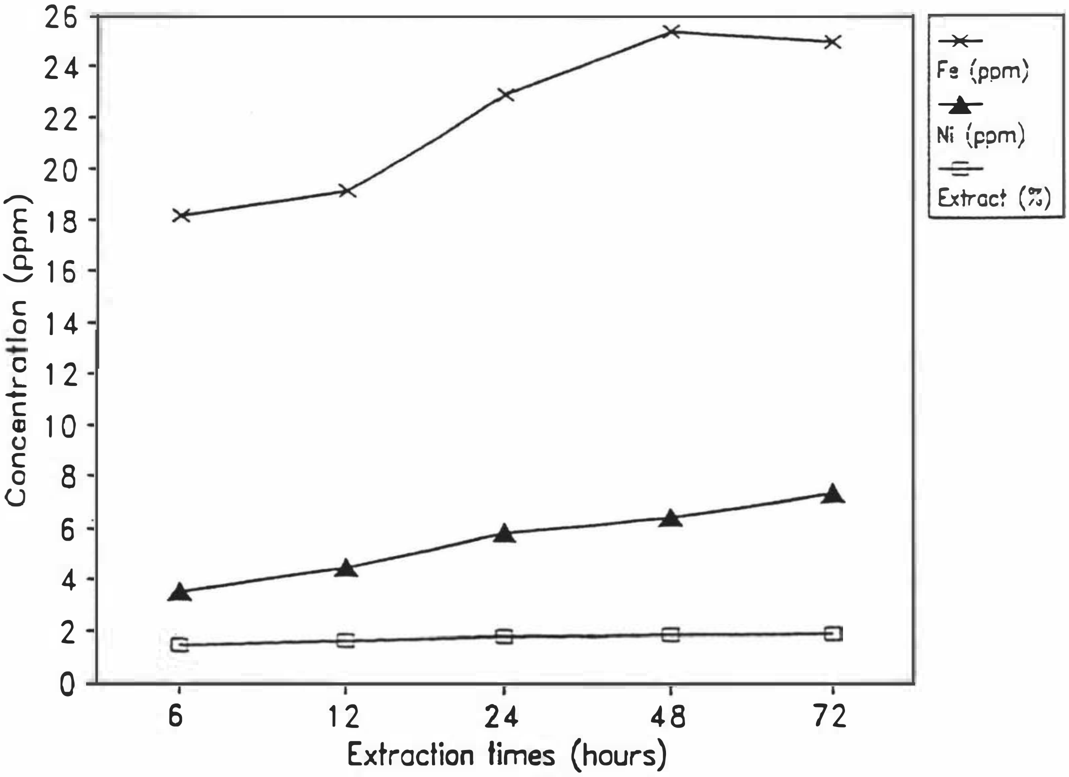


Table 3.11: Bitumen content (wt %) of rock and coal samples (sample details given in chapter 2.4.1)

Coal/Rock extracted	**Bitumen [%]**
Mangarakau	3.0
Maui-4	7.7
North Cape	3.2
Pritchard Bitumen	1.0
Pritchard carb. shale	2.0
Puponga	4.1
Toko A	3.7
Toko B	4.8
Toko C	6.1
Waipawa shale	0.3
Waipawa shale (Otoro Stream)	0.3
Yumen	0.3

C. Pyrolysis

The heating of kerogens, asphaltenes and rocks in a closed vessel (autoclave) in the presence of water (hydrous pyrolysis) generates hydrocarbons by thermal decomposition (*Tissot* and *Welte 1984, Miles 1989*). Pyrolysis of rocks rich in organic matter generates hydrocarbons which closely resemble natural crude oils (*Rowland et al. 1985, Lewan 1985*). Although the temperatures involved in pyrolysis experiments are higher than temperatures during natural crude oil generation, temperature can, to some extent, be substituted for time in experimental oil generation studies (*Rowland et al. 1985, Lewan 1985*). Pyrolysis in the presence of water helps to produce alkenes which are not formed if no water is added (*Lewan et al. 1979*).

Puponga, Mangarakau, Wairoa and North Cape samples were extracted with toluene/methanol (7:3) to remove any soluble organic matter (*van Berkel 1987*, *Filby* and *Fitzgerald, pers. comm.*). Samples were extracted for 4 hours in an ultrasonic bath with water temperatures kept at 30°C. After the removal of the solvents, the extracts were dried and weighed. Ultrasonic extraction can substitute for Soxhlet extraction and it has the advantage of short extraction times and low temperatures (*Blanco et al. 1992*). About 15 g of dry, extracted coal was weighed into a steel bomb and 15 mL of de-ionised water was added. The tightly closed container was heated to 300°C and kept at that temperature for 5 hours. After cooling, the sample was stirred and transferred to a glass beaker. The water was removed by filtration from the sample. The so-formed hydrocarbons and the pyrolysis water were analysed by ICP-ES to check trace element contents. A water blank was heated and filtered as described above and analysed by ICP-ES for contamination levels.

The dried coal samples were extracted with toluene/methanol and the solvents removed by rotary evaporation. The dried extracts (bitumen I and II) were analysed by INAA and the results are listed in Appendix F.

Trace element concentrations in the water blank were mostly below the detection limit of ICP-ES and only Fe, Na, K and S concentrations were detectable (2.0, 27.5, 28.5 and 4.4 µg/mL respectively). Small amounts of Mn (0.3 µg/mL), Ni (0.05 µg/mL) and Zn (0.08 µg/mL) were also detected. Iron and Mn are probably released from the steel container, whereas Na and K might have been present in the water or partly released from the coal. Small amounts of sulphur could have been formed during pyrolysis in the coal and consequently dissolved in the water.

D. Kerogen

Kerogen is the organic matter in sedimentary rocks that is insoluble in organic solvents and essentially is preserved organic material formed during the breakdown of plant and animal matter (*Miles 1989)*.

Kerogen is obtained by demineralising rocks with HF/HNO_3. Four coal samples (Mangarakau, North Cape, Puponga, Wairoa) were extracted as described for pyrolysis experiments and the samples were weighed into polypropylene beakers. The samples were heated with 6 M HCl for 4 hours, then the residue was filtered off and washed with diluted HCl. The sample was then heated with a 1:3 mixture of 6M HCl/HF for another 4 hours and the remaining sample filtered again. Then, 5 mL of 6M HCl was added, the sample heated and the final residue was filtered and washed with deionised water (after *van Berkel 1987)*. After drying at about 70°C, the sample was ashed at 550°C in a muffle furnace, the resulting ash dissolved in 2M HCl and was analysed by ICP-ES.

Demineralisation is usually carried out under a nitrogen atmosphere at a constant temperature of 60°C. As the necessary apparatus was not available, the treatment with HCl probably resulted in losses of trace elements as chlorides although the samples were boiled or taken to dryness. The analytical results are shown in Appendix I.

3.2 NEUTRON ACTIVATION ANALYSIS

Instrumental neutron activation analysis (INAA) is a non-destructive analytical method that has been used extensively in determination of trace element concentrations in geochemistry. It is especially useful in the study of trace elements in crude oils and their components.

3.2.1 PREVIOUS WORK

Filby and *Shah (1975)* investigated the use of INAA, its accuracy and precision, in the determination of trace elements in crude oils. They concluded that INAA is more accurate, less prone to error and suffers from fewer interferences than many other methods. Their results showed good agreement with NBS standards, whereas the analysis of the same NBS oil standard by different laboratories using spectrochemical methods such as atomic absorption, x-ray fluorescence and emission spectrometry resulted in a wide range of values.

Hitchon et al. (1975) used INAA to determine trace element abundances in 88 Canadian oils and to study the relationship between trace elements in oil and in the organic components. *Hitchon* and *Filby (1984)* measured 11 trace element concentrations in 75 crude oils from Alberta, Canada, grouping them into 3 families based on their metal contents. *Ellrich et al. (1985)* determined 12 elements in South German crude oils from 17 oilfields and *Hirner (1987b)* used INAA to study metal concentrations in asphaltenes, bitumens and kerogen to correlate oils and source rocks. *Jacobs* and *Filby (1983)* determined 30 trace element concentrations in oilsand extracts and were able to classify trace elements into organic and inorganic groups.

3.2.2 THEORY

Neutron activation analysis measures the radiation released during the decay of artificially generated radioactive isotopes. Samples are irradiated with thermal neutrons from a nuclear reactor, resulting in the formation of radioactive isotopes which disintegrate spontaneously to form stable nuclides. During this process, electromagnetic radiation and/or particles are released. The emitted electromagnetic γ-radiation is measured by a detector. A variety of detectors can be used, the most common being semiconductor or scintillation detectors. The γ-ray spectra obtained are characteristic for each element, as the rays are emitted at element-specific energies, and can be used to identify elements and their concentrations in samples.

3.2.3 ADVANTAGES, ERRORS AND PRECISION

The determination of trace element concentrations by neutron activation analysis has several advantages over other analytical methods.

It is a very sensitive method for many elements, allowing the detection of 10^{-5} µg amounts of some trace elements. Small samples can be used making the preconcentration of samples by wet or dry ashing unnecessary. This minimizes the risk of contamination and decreases the loss of volatile elements.

A range of trace elements can be determined simultaneously, cutting down on analysis time. It is a non-destructive method, and the risk of loss of volatile trace elements is minimised, as no high temperatures are required.

Interferences and errors are relatively small and mostly due to unequal neutron flux at sample and standard, differences in sample geometry of standards and samples, scattering and self shielding. For most elements, high precision can be obtained, as the relative standard deviation usually lies around 5% (*Filby and Shah, 1975*).

3.2.4 INSTRUMENTATION

The New Zealand and overseas oils, asphaltenes, and coal extracts were analysed at the Nuclear Radiation Center at Washington State University, Pullman, Washington State, USA using the TRIGA III-fuelled research reactor. A Ge(Li) detector interfaced with a ND 6620 spectrometer was used for γ-ray measurements. Several sample analyses were performed with participation of the author during a visit to the Nuclear Research Center, Washington State University.

3.2.5 SAMPLES AND ANALYSIS METHOD

Samples were analysed at a neutron flux of 6×10^{12} cm^{-2} s^{-1}. Two different irradiation times were used: 5 min for elements with very short and short half-lives and 8 hours for nuclides with intermediate and long half-lives. Elements determined, irradiation, decay and counting times, and half-lives are shown in Table 3.12.

New Zealand and overseas oil samples were used undiluted. Asphaltenes and coal extracts were analysed as solids and weighed directly into the polyethylene vials. Results are listed in Appendix A (New Zealand oils), Appendices B and C (overseas oils) and Appendix F (extracts).

Oil samples (200 to 400 mg) were weighed into small polyethylene vials; only about 50 to 100 mg of asphaltenes and extracts were used. The vials were heat-sealed and placed in a larger polyethylene vial which was also sealed. To ensure good and reproducible results, samples should not cling to the sides of the containers but be placed entirely at the bottom of the vials to ensure even sample geometry.

Three samples and one standard at a time were fastened on to a plastic rod, placed into the water basin above the reactor and irradiated. Fly-ash and coal (Research Center standards) were used as standards for oils and asphaltenes/extracts. The second polyethylene container was removed, the samples allowed to decay and they were then counted. The γ-ray peaks were recorded by computer and converted by an appropriate computer program to give element concentrations.

Thirty-seven trace elements were measured, but most New Zealand oils showed some elemental concentrations below the detection limit.

Table 3.12: Irradiation, Decay and Counting Times for Instrumental Neutron Activation Analysis

NUCLIDES	HALF-LIFE RANGE	IRRADIATION TIME	DECAY TIME	COUNTING TIME
^{28}Al, ^{47}Ca, ^{27}Mg, ^{51}Ti, ^{52}V	2.5-9.5 min	5 min	1 min	150 sec
^{38}Cl, ^{56}Mn,	35-160 min	5 min	30 min	1000 sec
^{76}As, ^{82}Br, ^{72}Ga, ^{42}K, ^{140}La, ^{99m}Tc (for Mo), ^{24}Na, ^{153}Sm	10-70 hrs	8 hours	36 hrs	4000 sec
^{131}Ba, ^{141}Ce, ^{60}Co, ^{51}Cr, ^{134}Cs, ^{152}Eu, ^{59}Fe, ^{181}Hf, ^{147}Nd, ^{58}Co (for Ni), ^{86}Rb, ^{122}Sb, ^{46}Sc, ^{75}Se, ^{182}Ta, ^{160}Tb, ^{233}Pa (for Th), ^{140}La (for U), ^{169}Yb, ^{65}Zn, ^{95}Zr	>4 days	8 hours	21 days	80000 sec

3.3. INDUCTIVELY COUPLED PLASMA EMISSION SPECTROMETRY

Inductively coupled plasma emission spectroscopy (ICP-ES) instruments were first made available in 1975 and since then a wide variety of geological and geochemical samples have been analysed. Mostly aqueous solutions are used although samples in organic matrices like crude oils and petroleum products have also been studied.

3.3.1 PREVIOUS WORK

ICP-ES has many applications and advantages as an analytical technique in geology and geochemistry (*Walsh* and *Howie 1986*), but only some work has been done using oil solutions.

Fabec and *Ruschak (1985)* used ICP-ES to determine Ni, V and S in crude oils and heavy crude oil fractions using organic solvents. They compared element concentrations obtained by ICP-ES with results from flame atomic absorption spectrometry studies. Precision (RSD of about 1%) and the agreement between both methods were very good. Their detection limits were as low as 0.1 µg/mL Ni and V. However, they encountered problems when using waxy oil samples, which had to be diluted in a different solvent system to ensure even nebulization and good burning characteristics. *Merryfield* and *Lloyd (1979)* studied wear metals in oils using ICP-ES and found it to be a rapid and precise multi-element analytical method.

3.3.2 THEORY

Emission spectrometry is based upon the line spectra produced by excited atoms and ions and the emitted radiation is used for quantitative analysis. The electrons of atoms are excited to higher orbitals and during the transition back to ground level state, radiation specific for each element is emitted. ICP-ES uses an argon plasma as the excitation source. The plasma is a conducting gaseous mixture of argon ions, electrons and, in small amounts, sample cations. The argon ions, once formed, absorb enough power from an external radio frequency generator to sustain a temperature sufficient for continuous ionization. The temperatures in the plasma core reach about 6000 to 10000 K. Sample solutions are nebulized and carried as droplets through the plasma by a stream of argon, where they are atomized. The characteristic radiation emitted by the sample cations and atoms is measured about 15-30 mm above the plasma core by a spectrometer. Figure 18 shows a diagram of a plasma torch.

3.3.3 ADVANTAGES, ERRORS AND PRECISION

The high temperatures in the plasma ensure complete decomposition of samples and minimize the interferences caused by ionization and molecular absorption. As the temperature cross section of the plasma is relatively uniform, self-absorption effects are not encountered, which makes it possible to obtain calibration curves of several orders of magnitude. Some instruments allow simultaneous multi-element analyses of samples, which reduces analysis time. Detection limits for some elements are better than with flame atomic absorption and lie in the 5-100 ng/g range for many elements.

Most instruments analyse only samples in aqueous solutions, as organic solutions require careful calibration, optimum flow rates have to be maintained and solvents can cause problems with tubing, leading to a change in the rate of sample take-up and consequently to erroneous results (*Fabec* and *Ruschak 1985*). Waxy samples prove even more difficult as they require a different solvent system for complete dissolution and even nebulization. The problems encountered with the solubility of waxy oils has led to erroneous results (*Fabec* and *Ruschak 1985*). The analysis of oil solutions additionally requires regular scrupulous cleaning of the torch and tubing to ensure accurate results.

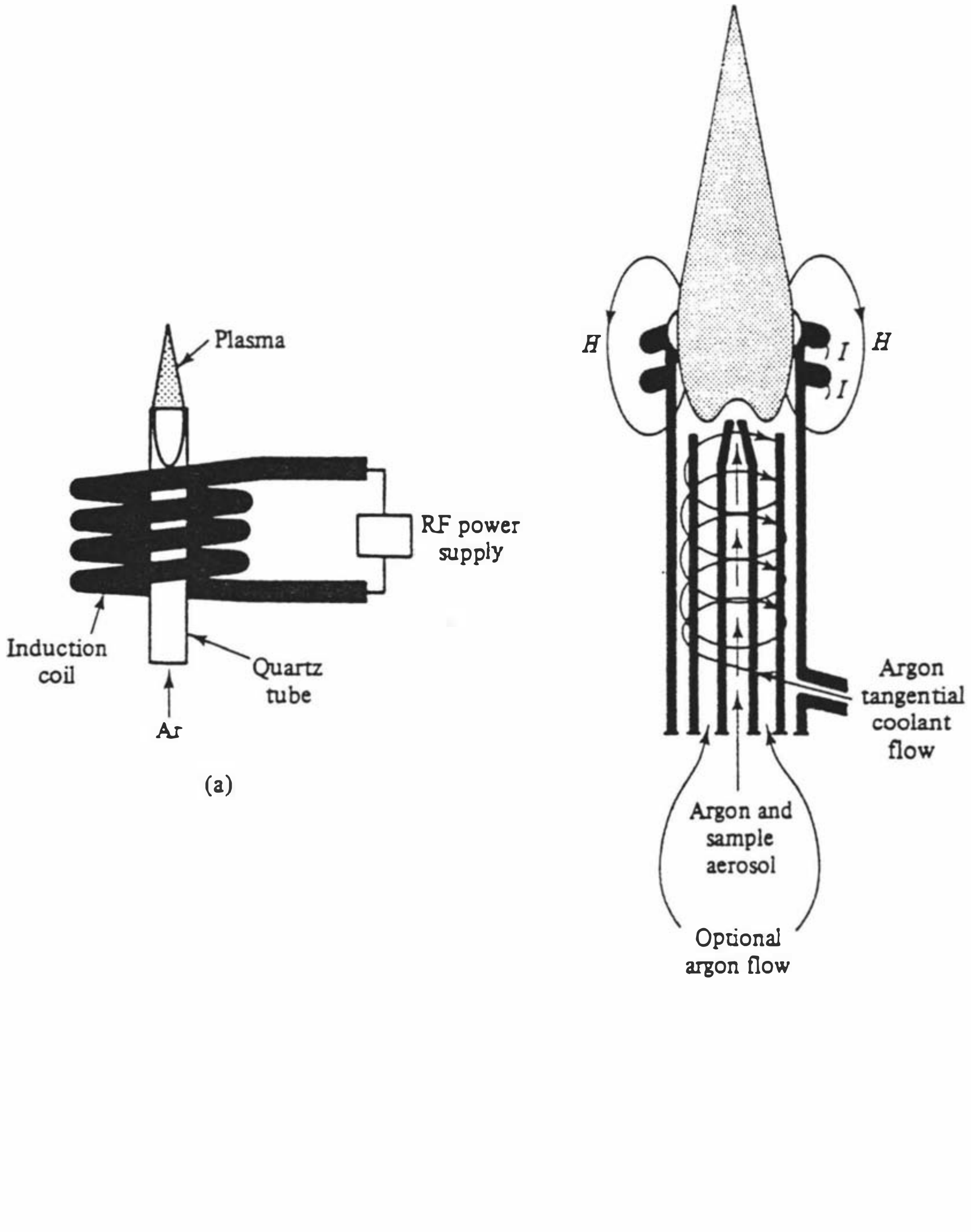
Interferences are caused by excess of certain trace element concentrations in the samples and high acidity of the solutions. Both problems can be easily overcome by dilution and by adjusting the acidity of the standard solutions. Matrix effects are usually lower than in other spectrochemical methods, if the sample and standard matrix are matched. The high temperatures in the plasma usually lead to complete destruction of the sample matrix. Interferences can occur at low analyte concentrations, due to the high background emission produced by the recombination of argon ions with electrons. A major problem is the spectral interferences encountered in the ICP-ES analysis.

3.3.4 INSTRUMENTATION

Two New Zealand oils were analysed by ICP-ES at the chemistry laboratory at Mobil, Seaview Terminal, Wellington. The instrument is used exclusively for the determination of wear metals in oils. Samples required only dilution by an organic solvent.

Additional ICP analyses were run at the Grasslands Research Centre, New Zealand Pastoral Agriculture Research Institute Ltd. (Crown Research Institute), Palmerston North.

Figure 18: Diagram of a plasma torch



(a)

3.3.5 SAMPLES AND ANALYTICAL METHOD

Sample solutions in organic solvents can be analysed with the Mobil ICP-ES instrument which is an advantage, as no pretreatment is required. Two New Zealand oils were studied to determine 20 trace element concentrations including Ni and V. Tuhua-2 and Stratford-1 oils were chosen as samples that are representative of the Taranaki Basin. As these oils are very waxy, they had to be diluted 5 times with the organic solvent to achieve lower viscosity and could then be directly introduced into the plasma. The dilution lowered sensitivity, causing problems detecting the low trace element concentrations.

The instrument at the Grassland Research Centre laboratory analyses only aqueous solutions and different oxidation and ashing procedures, as described in chapter 3.1.2, were tried for New Zealand oils and the resulting acidic solutions were analysed.

Coal samples were analysed in 2 M HCl solutions after ashing and pretreatment as described in chapter 3.1.4. Well water samples and the blank solution from the pyrolysis experiments were filtered twice through Whatman filter paper #542 and analysed without further treatment.

Samples are aspirated into the plasma. Readout and calculation of elemental concnetrations in the solutions are done by computer. Eighteen elements were determined, but unfortunately V could not be determined as the instrument does not have a vanadium channel.

3.4 GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY

Graphite furnace atomic absorption spectroscopy (GFAAS) was first introduced by L'vov and commercial electrothermal atomizers have been available since the 1970s. GFAAS has been extensively used in the determination of trace elements in a wide variety of samples. Its sensitivity makes it one of the best analytical methods for the determination of low levels of trace element concentrations in organic and aqueous solutions.

3.4.1 PREVIOUS WORK

The introduction of electrothermal atomic absorption spectrometry has been seen as a major advantage in the analysis of sample solutions in organic solvents and GFAAS has been applied to trace element determinations in oils, asphaltenes, bitumen, source rock extracts and oil products. The method was a big improvement on flame AAS as samples could be analysed directly after dilution or undiluted without the need for dry or wet ashing of the sample.

In 1971, *Omang* analysed mineral oils (diluted about 10 fold with xylene) to determine Ni and V concentrations. He ashed oils to compare results and found reasonable agreement between methods, although samples with low concentrations showed poor precision. His main problem was to control the spreading of the viscous solutions over the graphite tube which, when uncontrolled, led to low results.

Chuang and *Winefordner (1974)* and *Brodie* and *Matousek (1971)* determined seven trace elements in engine oils and lubricating oils using aqueous standards. Both claimed good agreement between organic solutions and aqueous standards.

Reeves et al. (1972) studied wear metals in engine oils. They found that GFAAS is an effective, simple, precise and accurate method for determining certain trace elements in oils, although analysis time was somewhat longer than for flame AAS.

As Ni and V are the most important trace elements in crude oils, considerable work has been done to study these elements and the problems connected with their analyses.

Barbooti and *Jasim (1982)* investigated the determination of V by electrothermal atomization and studied the interferences encountered. They reported considerable interferences by some elements, especially W which can form an extremely stable carbide compound with V.

Five trace elements in crude oils, oil extracts, asphaltenes and resin fractions were determined by *Zaki et al. (1989)* to study the concentrations of metals in the different fractions of oil and the distribution of Ni and V between porphyrinic and non-porphyrinic complexes.

Most trace element studies by graphite furnace atomic absorption spectrometry have been done on relatively heavy crude oils with elemental concentrations in the µg/g range. *Bruhn* and *Cabalín (1983)* were the first to analyse low levels of Ni in gas oils. They generally found good precision, although they experienced loss of Ni during the ashing cycle in the analyses of some oils. The ashing temperature has to ensure complete destruction of the organic matrix without losing the volatile nickel compounds in the oils. This adjustment is made difficult as no information about the nature and volatility of the Ni complexes in gas oils is available.

Graphite furnace atomic absorption spectrometry is a precise and accurate method for determining trace elements in oils but numerous interferences and matrix effects do exist. Vanadium especially, is difficult to measure as peak tailing and possible reactions with the graphite carbon can occur. *Wendl* and *Müller-Vogt (1985)* and *Manning* and *Slavin (1985)* studied V and its possible reactions in the graphite tube, but concluded that no side reactions should exist above 2000 K and V should be present as atoms above this temperature.

3.4.2 THEORY

Atomic absorption spectroscopy is based upon the measurement of radiation absorbed by gas phase atoms when electrons move from electronic ground state to higher orbitals. The absorbed energies are characteristic of different electron transitions in specific elements. The production of gas phase atoms is usually achieved by aspirating the sample solution into a flame.

In GFAAS analysis the flame is replaced by a graphite tube held by two graphite electrodes. The graphite furnace is heated electrically in stages: drying, ashing and atomizing. The samples are atomized at high temperatures (up to 3000°C). The radiation source is a hollow cathode lamp and a D_2 lamp is used for background correction.

3.4.3 ADVANTAGES, ERRORS AND PRECISION

Graphite furnace atomic absorption is a very sensitive method. Small volumes can be used and samples can be analysed without the need of ashing. The use of organic solvents is more problematic and prone to errors compared to the use of aqueous solutions.

Only one element at a time can be measured making it a relatively time consuming procedure if a large number of samples and elements are to be studied.

Electrothermal atomic absorption is prone to many interferences. Scattering and molecular absorption produced by incompletely atomized particles are spectral interferences frequently experienced in the analyses of organic sample solutions. They can be corrected by the use of a D_2 lamp (background correction). Chemical interferences are also common in GFAAS work. Peak heights can be affected by an interfering element or compound in the sample matrix, leading to wrong results. The chemical form of the analyte after the evaporation of the solvent and salts can greatly influence atomization efficiency, shape and appearance time of the peaks.

Most chemical interferences can be minimized by extraction of metals or destruction of the matrix. However, this may not always be a feasible solution, especially when organic samples are concerned.

Precision is influenced by sample matrix effects and other possible interferences, and RSD usually lies in the 1-5% range. Detection limits for many elements are in the ng/g range, but the method is less sensitive for carbide forming elements such as V.

3.4.4 INSTRUMENTATION

The instrument used for all organic sample solutions was a GBC system 1000 furnace unit, coupled to a GBC 902 AA spectrometer as depicted in Figure 19. Sample injections were done by a PAL 1000 automatic sampler. The absorption peaks were printed by an Epson LX-80 dot matrix printer. Peaks were recorded as peak heights or areas, although accurate peak measurements were performed by hand to avoid errors caused by a shifting baseline.

The pyrolytically coated graphite furnace is a 9 mm long tube with an inner diameter of about 3 mm and is held by two graphite electrodes shown in Figure 19. The electrodes are connected to water-cooled steel blocks.

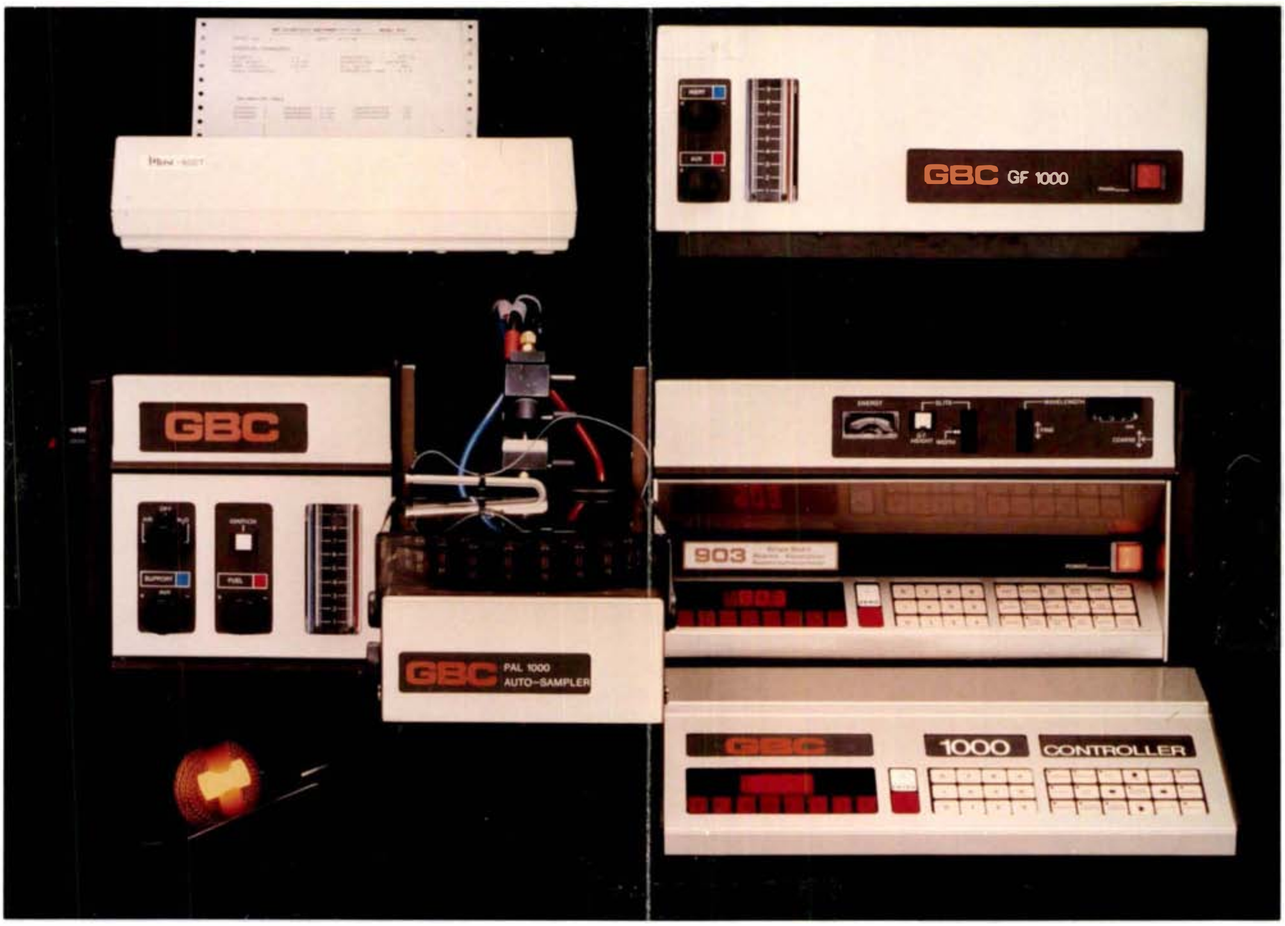
During the heating cycle, a flow of oxygen-free nitrogen shields the sample from the surrounding atmosphere to prevent possible reactions with oxygen thus decreasing interferences and increasing sensitivity.

The V determinations in ashed oil and coal samples were performed with a GBC system 2000/3000 instrument connected to a GBC 909 atomic absorption spectrometer. The peaks and programs were recorded and stored in a computer connected to the system. Concentrations of sample solutions were calculated automatically using the previously recorded standard curve.

The graphite tube is 25 mm long and fully enclosed in a steel case. An inert atmosphere is created in and around the graphite tube by a flow of oxygen-free nitrogen during the heating cycles. This reduces wear of the graphite tube and prolongs its life-time. The increased size of the graphite tube allows the use of larger sample volumes, up to 50 µL per injection.

Single element hollow cathode lamps were used in both instruments as radiation sources. Lamp currents were kept as low as background noise and sensitivity allowed, to increase the life of the lamp and decrease possible self-absorption effects.

Figure 19: GBC System 1000 with AAS 902 and graphite furnace head



Background absorption was used whenever possible to correct for molecular absorption by the element and by the organic oil matrix.

3.4.5 STANDARDS

A. Organic standards

Two NBS standard oils were used in the determination of trace element concentrations in oil samples.

NBS standard 1634b is a commercial residual fuel oil with eight certified trace element concentrations. Eight provisional trace element values are additionally reported for information only. The second standard is the NBS 8505 oil, a Venezuelan crude oil with a certified V concentration. Trace element concentrations are listed in Table 3.13.

Table 3.13: Trace element content of NBS standard oils.

	NBS 1634b	**NBS 8505**
As (µg/g)	0.12 ± 0.02	
Co (µg/g)	0.32 ± 0.04	
Fe (µg/g)	31.6 ± 2.0	
Mn (µg/g)	0.23 ± 0.03	
Ni (µg/g)	28.0 ± 2	
Se (µg/g)	0.18 ± 0.04	
V (µg/g)	55.4 ± 1.1	390 ± 10
Zn (µg/g)	3.0 ± 0.2	

Both oils were stored in tightly sealed and refrigerated glass bottles. They were allowed to warm to room temperature for about one hour before sampling. Both standards were stirred with a glass rod and samples were taken from the upper half of the standard as recommended in the materials handling section of the NBS report. The standards were usually weighed into a flask and diluted with analytical grade toluene to obtain solutions for a standard curve that matched the sample concentrations.

The Venezuelan standard was analysed twice by neutron activation analysis and values for major trace metals agreed favourably within the two analyses, except for Fe (Table 3.14). Graphite furnace results, calculated by using the fuel oil as standard, showed equally close agreements. The Venezuelan oil was then employed as an additional second standard (except for the determination of Fe) for the quantification of trace elements in oils by GFAAS.

Table 3.14: Instrumental NAA analysis of a Venezuelan standard oil

	1st INAA analysis	**2nd INAA analysis**
Co (ng/g)	697 ± 32	665 ± 35
Fe (µg/g)	18.9 ± 2.9	9.4 ± 2.8
Mn (ng/g)	746 ± 47	759 ± 48
Ni (µg/g)	55.4 ± 3.0	48.7 ± 8.3
V (µg/g)	367.0 ± 23	386 ± 28

Solutions of higher concentrations were prepared about once a week and refrigerated. Working solutions were prepared daily by dilution. This was necessary as an appreciable amount of toluene evaporates at room temperature and even after storage in the refrigerator. This results in altered standard concentrations leading to possible erroneous results.

B. Aqueous standards

Aqueous standards, when used, were prepared by dilution of 1000 µg/mL stock solutions (BDH where available).

Aqueous stock solutions (1000 µg/mL) for Al, Pb and Bi were prepared from analytical-grade metal (Pb, Al) or chemical compounds ($Bi(NO_3)_3$) and dissolved according to standard procedures (GBC handbook for AAS). Standards were diluted to the appropriate concentrations by dilute HCl or HNO_3.

Stock solutions (10 µg/g) of standards in isopropanol/toluene were prepared using aqueous 1000 µg/mL standards and stored in the refrigerator. Working solutions were then prepared daily by dilution with the solvent mixture. This was necessary as solutions at low concentrations (below 5 µg/mL) deteriorated quickly. Usually no signals could be obtained if the solutions were older than 48 hours, irrespective of the element concerned. This could be probably due to precipitation, salt formation or adhesion of the compounds in solution to the glass wall of the compounds in solution, as shaking and slight heating of the solution resulted in recovery of part of the dissolved metals.

3.4.6. SAMPLES AND ANALYTICAL METHOD

All organic oil, asphaltene and extract solutions were analysed with the GBC system 1000/GBC AAS 902, whereas V in ashed oil and coal solutions was determined using the GBC 2000/3000.

A. Oil samples

The trace element analysis of New Zealand and overseas crude oils by GFAAS proved difficult, as the oil solutions in toluene, especially the light and waxy New Zealand oils, are highly viscous. The solutions tended to spread over the inside and outside of the graphite tube and sample losses of up to 50% were experienced. Spreading was not a problem in the analyses of asphaltene solutions, as they were highly diluted by toluene and did not contain any light and volatile organic compounds.

The injection of small sample volumes of 1 µL decreased the spreading of the solution. The spreading could additionally be controlled by heating the furnace to 80°C before the injection of the solution, to evaporate highly volatile and viscous compounds. The temperature was then quickly raised to 150°C, with a heating rate of about 4°C/s, to evaporate the solvent and any remaining volatile oil compounds. Faster heating led to the loss of sample as the oil exploded inside the furnace. The precise adjustment of the injection tip is also important to avoid the loss of solution. The tip was adjusted so it did not touch the sides of the graphite tube and was positioned slightly above the bottom of the graphite tube. If the tip touched the bottom wall of the heated tube, part of the sample crept up the plastic tube and was lost.

Decreasing the viscosity of the liquid by adding two to three drops of silicone oil to 2 mL of sample solution increased the signal height by 30% to 50%, dependent on the dilution of the oil. The Si oil was checked for contamination by analysing a solution of Si oil in toluene. No measurable amounts of Co, Fe, Mn and Ni were detected. Si oil was added to all oil solutions in toluene before analysis.

Correct trace element concentrations could only be obtained with standards that matched the sample matrix very closely. Inorganic salt standards in aqueous solutions resulted in a very different standard curve than organic oil standards (Figure 20). This is mainly due to the different spreading behaviour of the viscous oils solutions.

Signal heights and shapes for all elements depended strongly on the condition of the graphite tube. Used furnaces with worn coatings often led to decreased signal heights with multiple peaks, as the sample solution was absorbed by the graphite and only slowly released. Figure 21 shows the Ni peaks of one oil solution obtained by both new and worn furnaces. Standards were analysed regularly after five to ten sample solutions to check changes in signal height or shape.

All trace element results determined by GFAAS were calculated using the mean of four peaks. Toluene and isopropanol/toluene blanks were analysed alongside oil or asphaltene samples to check contamination levels of the solvent and possible memory effects of the furnace tubes.

Figure 20: Nickel and Fe standard curves obtained with fuel oil and aqueous solutions

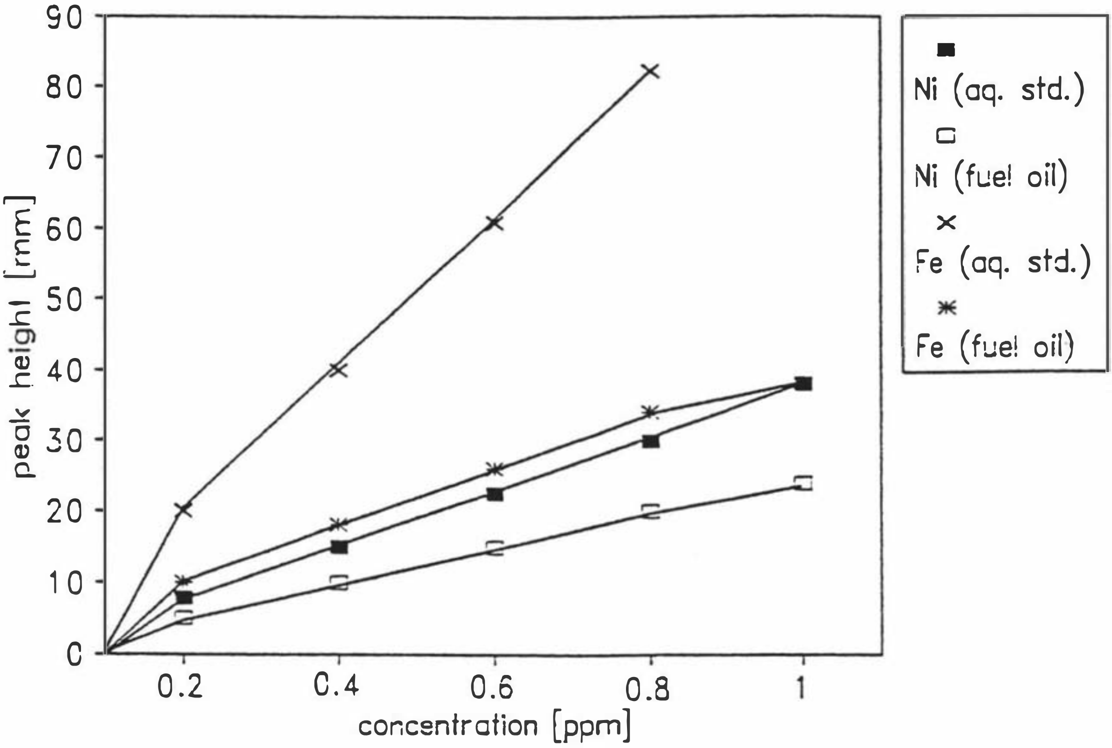
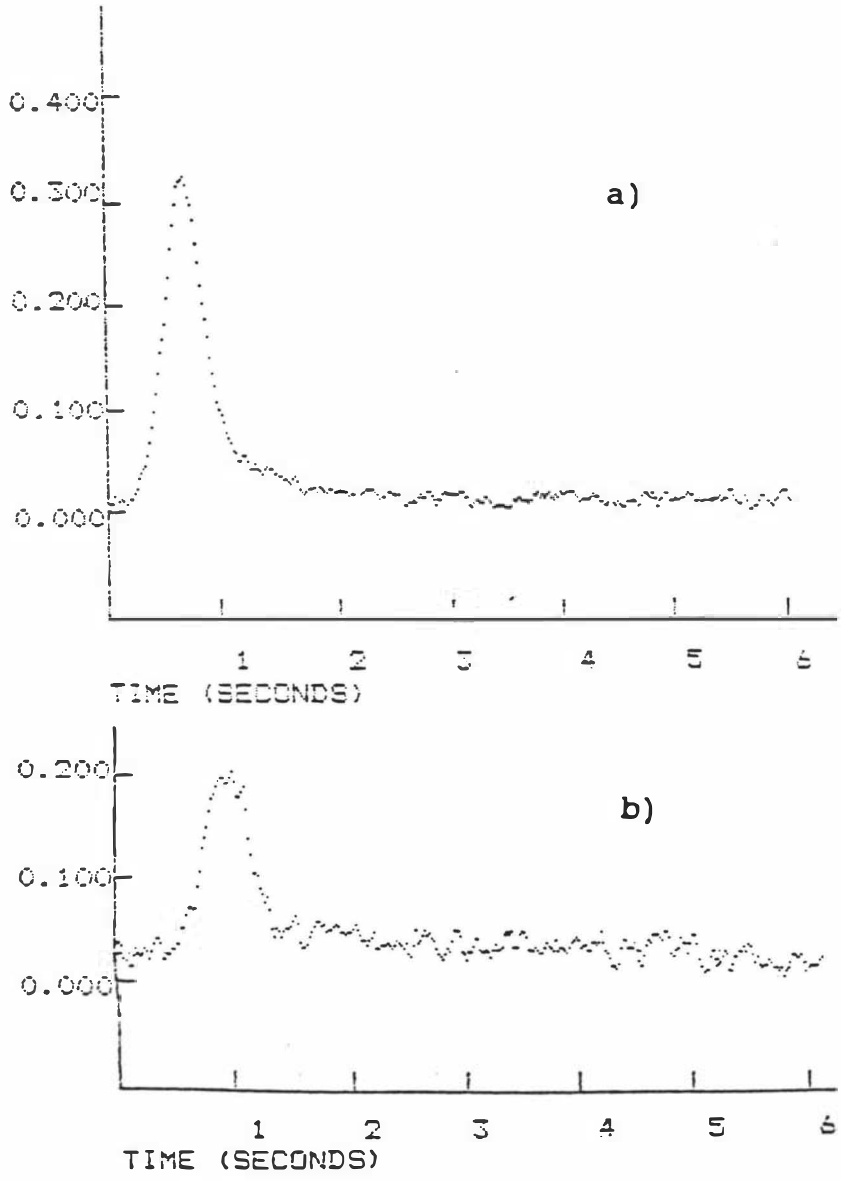


Figure 21: Nickel peaks in new (a) and worn (b) graphite furnace tube (identical concentrations)



The Zn concentrations in the toluene blank were above the detection limit and blank values were therefore subtracted from the oil sample concentrations.

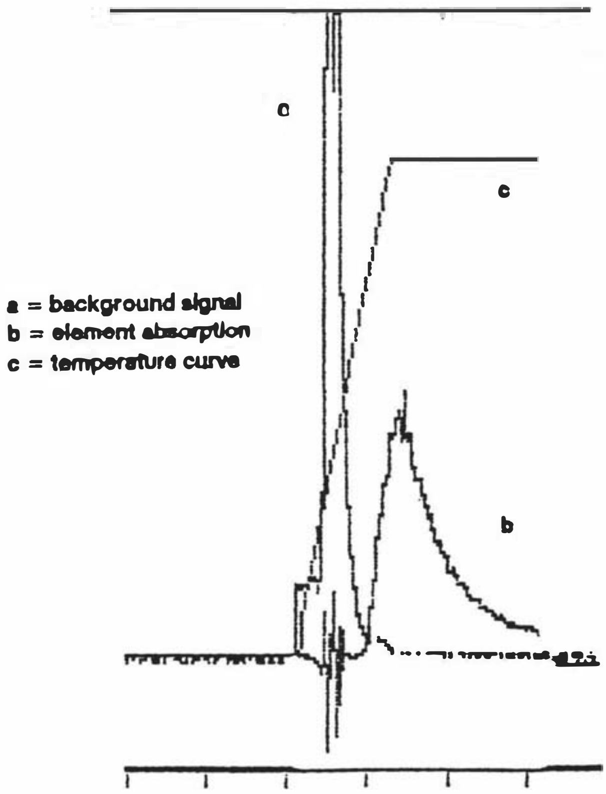
B. Heating programs and wavelengths

All elements were analysed using the most sensitive absorption wavelengths (Table 3.15). If the element concentrations in the samples were too high, solutions were diluted as necessary. Nickel was analysed using the 341.5 nm line, as the resulting standard curve was less curved and the signal more stable. Background correction was used whenever possible in the analyses of all toluene and isopropanol/toluene sample solutions. One oil sample was analysed for Ni with the GBC system 2000/3000 to check for possible interferences by organic material or other elements, as element and background absorption can be distinguished by the GBC system 2000/3000. Background absorption was significant but it was recorded well before the Ni peak and did not interfere (Figure 22).

Table 3.15: Wavelengths used for the determination of trace elements by GFAAS

	Wavelength [nm]		**Wavelength** [nm]
Cd	228.8	Mn	279.5
Co	240.7	Ni	341.5 (232.0)
Cu	324.8	Pb	217.0
Fe	248.3	Zn	213.9

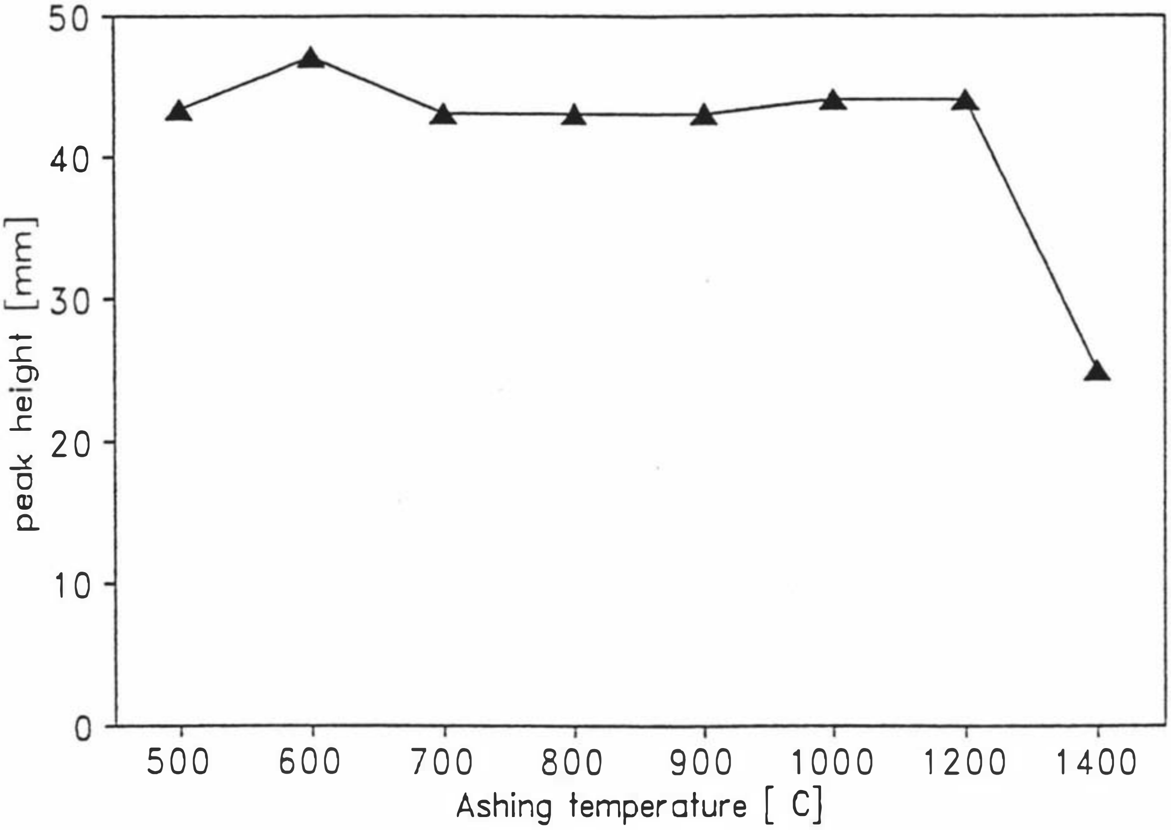
Figure 22: Nickel absorption peak with recorded background absorption (GBC system 2000/3000)



A drying temperature of 150°C was used for all toluene and isopropanol/toluene solutions, as the solvents (toluene b.p. 111°C, isopropanol b.p. 82°C) and most of the highly volatile compounds were removed at this temperature. The samples were kept at 150°C for 15 sec and the furnace was then heated to the required ashing temperature at a rate of about 20°C/s.

Ashing temperatures below 600°C did not char the organic matter completely. Smoke and incompletely ashed matter could interfere with the signal. To find an ideal ashing temperature that charred the oil matrix, but did not lead to trace element losses, one sample was analysed for Ni at varying ashing temperatures. Figure 23 shows the resulting Ni peaks. This procedure was repeated for other trace elements.

Figure 23: Absorption peak heights for Ni in oil solutions at different ashing temperatures



Samples were kept at the ashing temperature for a minimum of 15 s. Cadmium and Pb signals were studied for interferences from smoke or incompletely ashed organic matter with the GBC system 2000/3000, as ashing temperatures had to be kept at 500°C to avoid the loss of the element. The observed background absorption did not interfere in the analysis. The accuracy of the obtained results was checked by analysing three samples by standard additions. The peaks increased in height as expected and concentrations obtained by standard additions agreed with GFAAS results within a 10% error margin.

Atomizing temperatures recommended by the GBC operation manual were chosen for most elements. The atomizing temperature for Fe was raised to 2500°C, as it resulted in more stable peaks and consistent heights. A complete list of drying, ashing and atomizing temperatures is given in Table 3.16. The samples were heated to atomizing temperatures at the fastest possible heating rate of 2000°C/s) and atomized for 3 s.

Table 3.16: Drying, ashing and atomizing temperatures used in the determination of trace element by GFAAS

	Drying Temp. [°C]	**Ashing Temp. [°C]**	**Atomizing Temp. [°C]**
Cd	150	500	1800
Co	150	600	2400
Cu	150	600	2200
Fe	150	600	2500
Mn	150	600	2400
Ni	150	600	2400
Pb	150	500	2000
Zn	150	600	1600

Germanium and Bi are enriched in coals by factors of 330 and 100 times respectively, when compared to their average content in the earth's crust (*Mason* and *Moore 1982*). Detectable amounts in New Zealand oils and asphaltenes could help to confirm coal source rocks, but Bi levels were below the detection limit. Coal ash was dissolved in HNO_3 or HBr instead of HCl, as $GeCl_4$ is highly volatile. The analysis of Ge in coal ash solutions was difficult due to matrix interferences. Extractions of the HBr solution with CCl_4 were not successful. Germanium concentrations in NZ oils and asphaltenes were below the detection limit even when multiple injections were used. Gallium porphyrins have been detected in coals (*Bonnett* and *Czechowski 1980*), and oils and asphaltenes were examined for their Ga content. Gallium concentrations determined by INAA were below the detection limit and GFAAS analyses was hindered by the organic matrix which was not destroyed by the low ashing temperature of 400°C and no measurable amounts were detected.

C. Vanadium determination

Vanadium was determined in aqueous solutions and the analyses were performed using the GBC system 2000/3000. Inorganic V standards in 2M HCl were used and the standard curve is shown in Figure 24.

Sample solutions had to be diluted, as V signals showed extreme tailing at concentrations above 1 µg/mL (Figure 25). After dilution, replicate determinations could be made with RSD of less than 10%. Marine oil samples were diluted 10 to 20 times and New Zealand oil samples were analysed undiluted. Coal ash solutions were diluted up to 100 times (Pritchard bitumen). The V lamp was run at 25 mA and the 318.4 nm line was used. An ashing temperature of 600°C and atomizing temperature of 2700°C were chosen. The 0.5 µg/mL standard solution was analysed during the sample runs to check for memory effects or possible element losses through absorption. The resulting concentrations of the standard varied between 0.48 and 0.54 µg/mL and details and results of the analysis are given in Chapter 3.1.2.

Figure 24: Vanadium standard curve (0.1 µg/mL, 0.2 µg/mL, 0.5 µg/mL and 1.0 µg/mL V in 2 M HCl)

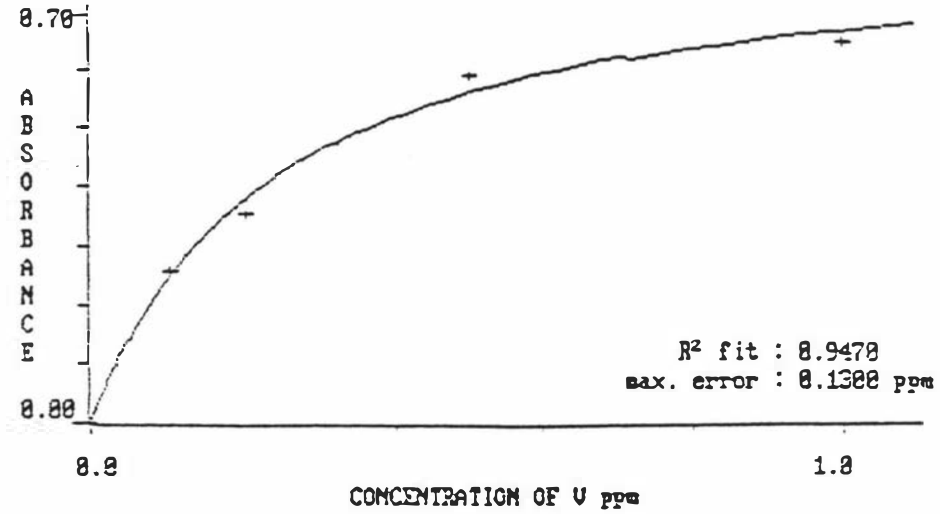
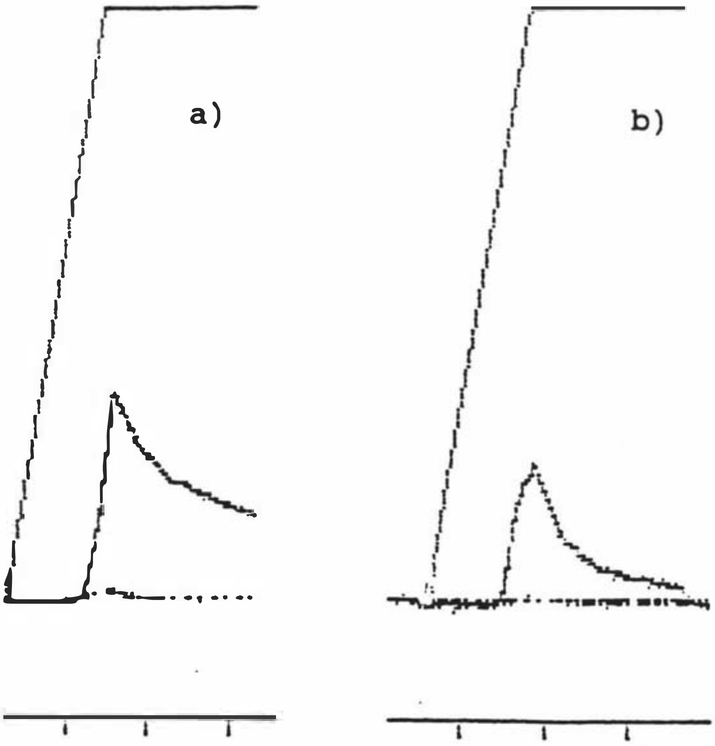


Figure 25: Tailing of V absorption peaks at high element concentration (a) compared to absorption peak obtained at low concentration



IV. RESULTS AND DISCUSSION

4.1 TRACE ELEMENT CONCENTRATIONS AND INTER-ELEMENTAL CORRELATIONS IN NEW ZEALAND OILS

A total of 42 elements -

Al, As, Ba, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Eu, Fe, Ga, Hf, Hg, K, La, Lu, Mg, Mn, Mo, Na, Nd, Ni, Pb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Ti, U, V, W, Zn, Zr, Yb -

was determined in New Zealand crude oils and condensates by GFAAS and INAA. Of these, 22 concentrations were below the detection limit and are not included in the discussion of results and statistical analysis. All trace element concentrations in New Zealand oils are shown in Appendix A.

New Zealand oils contain only low amounts of most trace elements, mostly in the ng/g range. Trace element concentrations in condensates are generally lower than in crude oils, as condensates are light oils with a low content of polar components that are able to complex metals and other elements. The range of trace element concentrations in New Zealand oils is shown in Figure 26.

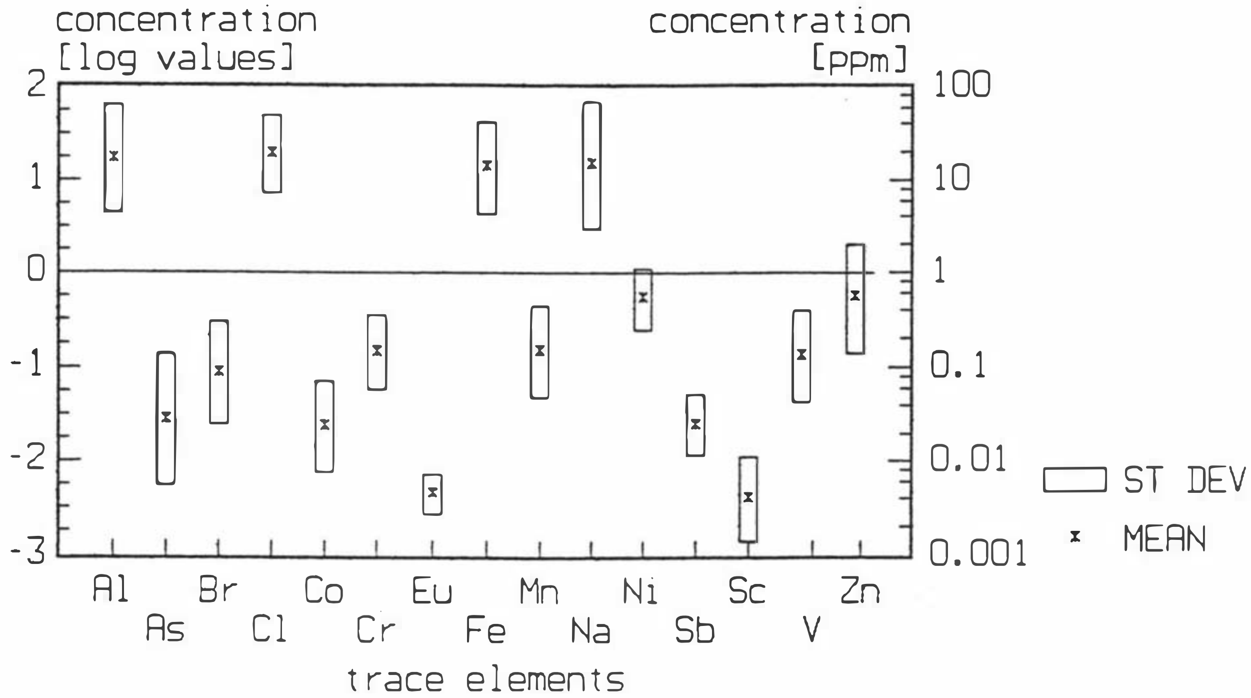
Trace element concentrations in seep oils can vary considerably as the INAA analysis of two independently sampled Waitangi oil samples shows (Table 4.1). The variations are mainly due to contamination or differences in composition caused by the evaporation of light hydrocarbons.

Contamination of crude oils during production and storage is possible as most samples were not directly collected from the point of production. Many of the oils were stored in large metal containers and metals could have leached into the samples, although most New Zealand oils are solid at the low storage temperature used.

Table 4.1: Variations in trace element concentrations in Waitangi Seep oil samples

	Al [µg/g]	Co [ng/g]	Fe [µg/g]	Mn [ng/g]	Ni [µg/g]	V [ng/g]
I	69.4	12.2	167.0	460.0	0.32	142.8
II	113.8	7.6	65.7	145.6	0.32	463.9

Figure 26: Range of trace element concentrations in New Zealand oils (log values and standard deviation)



Comparison of two oils (Tuhua-2 and Stratford-1), which had been stored and sampled from metal containers and additionally from a glass container did not show any significant variations in most metal concentrations (Table 4.2), although Al values in the Tuhua-2 oil samples varied by about 50%. This is probably due either to variations in composition throughout the oil or in the amounts of finely dispersed inorganic matter in the samples.

Table 4.2: Trace element concentrations in oils stored in glass and metal containers

	Tuhua-2		**Stratford-1**	
	Glass	Metal	Glass	Metal
Al (µg/g)	13.7	5.0	65.3	70.1
Cr (ng/g)	169.0	88.9	314.0	282.0
Fe (µg/g)	7.1	7.3	25.7	28.6
Mn (ng/g)	80.0	68.6	193.0	290.0
Ni (µg/g)	11.3	9.9	57.8	60.6

The study of trace element concentrations in crude oils is also based on the assumption that the trace element contents in oils from one well do not vary significantly throughout the production period or with hydrocarbon depth in the reservoir, as usually only one sample is analysed.

4.1.1. Nickel and Vanadium

The Ni and V contents of analysed New Zealand oils are very low and most values are in the ng/g range. The average Ni concentration in 47 New Zealand oils is 0.69 µg/g, with Ni values ranging from 0.12 µg/g (Pukemai-2 condensate) to 2.87 µg/g (Kora-1). As biomarker studies of the Kora-1 oil show marine influence for this oil (*Reed 1991*), the higher element concentration could reflect this. Moki-1, Maui-1, Pukearuhe-1, Urenui-1 and Kotuku seep oils have relatively high Ni concentrations of 1.26 µg/g, 1.47 µg/g, 1.68 µg/g 1.50 µg/g and 1.36 µg/g respectively. The high value in the Pukearuhe-1 oil sample possibly reflects a marine influence on oils from this location in North Taranaki Basin. The oil is possibly sourced from older marine/deltaic rock *(Collen, pers. comm.)*.

The V content in all New Zealand crude oils is a definite indication of the terrestrial landplant source, as the average V concentration is 217 ng/g with values ranging from as low as 15.8 ng/g (Kaimiro-1 condensate) to 647 ng/g (Pouri-1). Although the Kora-1, Pukearuhe-1 and Waitangi Seep oils are considered to show a marine influence, their V content is as low as in other Taranaki crude oils.

Crude oils low in sulfur, with an asphaltene content of about 0.1% and derived from terrestrial material with high input of landplant matter usually contain low concentrations of Ni and V (*Barwise 1990)*, regardless of maturity. Nickel is frequently prevalent over V in these oils (*Tissot* and *Welte 1984*). New Zealand oils contain very little V and Ni, with Ni prevalent over V following the trend of other terrestrial, high paraffin oils.

Both elements were used in various studies to determine migration patterns or to distinguish oils from different source rocks and geographical areas. A plot of Ni versus V for New Zealand oils (Figure 27) does not allow for differentiation of the oils. Only one of the Kora-1 oil samples lies distinctly separate on the plot due to its high Ni content. The Pukearuhe-1, Maui-1 and Kotuku seep oils lie slightly separate from other oils on the graph and most condensates are scattered at the lower end of the scale. All oils from the McKee field contain less than 1 µg/g Ni concentration, but their V values vary considerably, spreading the oils randomly throughout the graph. Moturoa, Republic-1 and Republic-4 oils lie very close in the graph and they are all produced from shallow reservoirs in the same area. The Taranaki-5 oil has a very similar Ni content, but is separated from the group by its higher V content. Large variations in the V values are partly due to the large errors involved in the difficult analysis of this element and to its extremely low concentrations. Figure 27a shows variations of Ni and V in oils from the McKee Field.

LEGEND

1	Ahuroa-2
2	Blackwater
3	Galleon-1
4	Kaimiro-1
5	Kapuni-1
6	Kora-1, DST2
7	Kora-1, DST3
8	Kotuku Seep
9	Kupe South
10	Kupe-2
11	Kupe-3
12	Kupe-4
13	Kupe-5
14	Maui-1
15	Maui-3
16	Maui-4
17	McKee-1
18	McKee-2
19	McKee-3A
20	McKee-4
21	Moki-1
22	Moturoa
23	Pouri-1
24	Pukearuhe-1
25	Pukemai-1B
26	Pukemai-2
27	Republic-1
28	Republic-4
29	Stratford-1
30	Stratford-1
31	Taranaki-5
32	Tariki-1
33	Tariki-1A
34	ToeToe-1
35	ToeToe-2B
36	ToeToe-3
37	ToeToe-4
38	Toru-1
39	Tuhua-1
40	Tuhua-2
41	Tuhua-2, A-Sand
42	Tuhua-2, B-Sand
43	Urenui-1
44	Waihapa
45	Waiotapu Seep
46	Waitangi Seep

Well	
McKee-1	Mc-1
McKee-2	Mc-2
McKee-3A	Mc-3A
McKee-4	Mc-4
Pouri-1	P-1
Pukemai-1B	P-1B
Pukemai-2	P-2
ToeToe-1	TT-1
ToeToe-2B	TT-2B
ToeToe-3	TT-3
ToeToe-4	TT-4
Tuhua-1	T-1
Tuhua-2	T-2
Tuhua-2, A-Sand	T-2
Tuhua-2, B-Sand	T-2

Figure 27: Nickel (µg/g) versus V (ng/g) for New Zealand oils

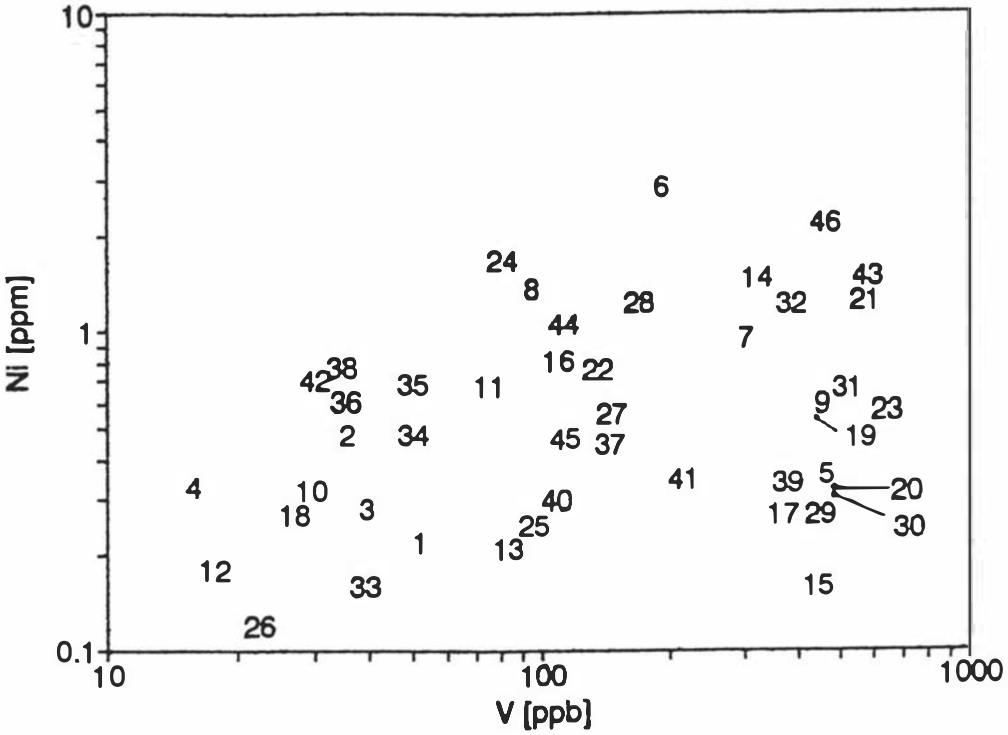
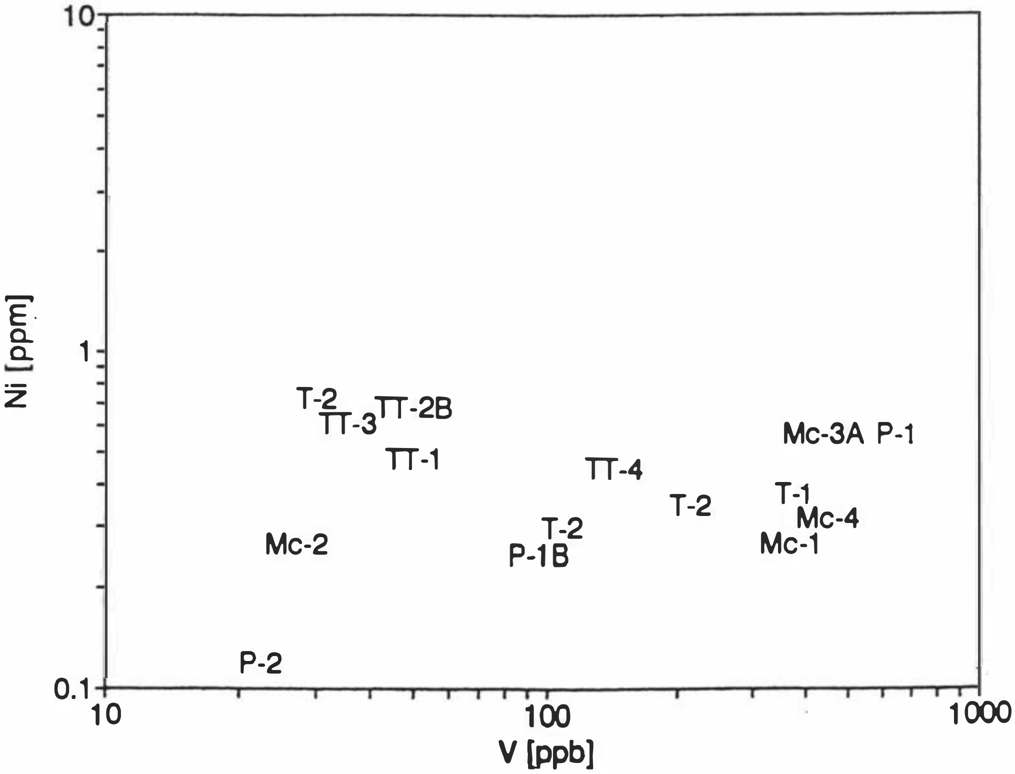


Figure 27a: Nickel (µg/g) versus V (ng/g) for oils from the
McKee Field



Errors have a relatively large effect, as values are in the ng/g range with oils containing about one third less V than Ni. The Ni and V concentrations in the Maui-1 oil range from 1.08-1.86 µg/g and 0.38-0.51 µg/g respectively, if instrumental errors are taken into account. Large variations among oils from the same field can be observed, although errors involved should be lower than the variations observed.

The V/Ni ratio used by *Al-Sharistani* and *Al-Atyia (1972)* in studying migration pathways, supplies little information for New Zealand oils, as ratios for the latter vary between 0.04 to 2.78, with no trend apparent. Oils from the McKee Field show V/Ni ratios of 0.04 to 1.34 (Table 4.3) with some subgroups visible, although ratios of oils from other fields are very similar. The large variations in the ratios cannot be attributed to differences in maturity levels as biomarker studies confirmed similar maturity levels for all oils from Taranaki Basin. The Tariki-1 and Ahuroa-2 condensates have a V/Ni ratio of 0.24, a good agreement as they both originate from the same field. All V/Ni ratios are listed in Appendix D.

The Ni/V ratio has been used for oil-oil correlations and discrimination of oils from different sources in numerous studies (*Hirner 1987, Curiale 1987, Branthaver* and *Filby 1987*). New Zealand oils show large variations in the Ni/V ratio ranging from 0.6 to 23.7. Even the Ni/V ratios of oils from the McKee field (listed in Table 4.3) differ considerably.

A plot of API gravities (*Robertson Research 1984, Cook 1987)* versus Ni+V concentrations (Figure 28), separates the Maui-1 and Moki-1 oils from other Taranaki oils, but not the Maui-4 oil. Condensates (Blackwater-1 and Maui-3) lie slightly separate, due to their high API gravities. The trace element content in oils from the same field decreases slightly with increasing API gravity, as lighter oils contain less polar compounds.
The graph supplies little information about other oils, as the number of oils with known API gravities is limited.

A plot of the S concentrations *(Cook 1987, Hirner* and *Robinson 1988*) versus V (Figure 29) clearly separates the Waiotapu Seep oil from other samples, as it contains about 20 times more S than other oils.

Table 4.3: V/Ni and Ni/V ratios in oils from the McKee Field

Well	Ni/V	V/Ni
Tuhua-2, B-Sand	23.7	0.04
ToeToe-1	9.6	0.10
ToeToe-2B	13.8	0.07
ToeToe-3	17.3	0.06
McKee-2	10.0	0.10
ToeToe-4	3.2	0.32
Tuhua-2	2.8	0.36
Pukemai-1B	2.6	0.38
Tuhua-2, A-Sand	1.6	0.61
McKee-3A	1.3	0.77
Pouri-1	0.9	1.14
Tuhua-1	0.9	1.11
McKee-4	0.7	1.39
Pukemai-2, cond.	5.4	0.19

The Pouri-1 sample is slightly separated from other oils due to its relatively high V concentration. Condensates and the McKee-2 oil lie towards the lower end of the scale. Oils from related fields contain similar amounts of S, but vary widely in their V content.

LEGEND

B	Blackwater Condensate
K	Kaimiro-1 Condensate
Kap	Kapuni-1
KS	Kotuku Seep
M-1	Maui-1
M-3	Maui-3 Condensate
M-4	Maui-4
Mc-1	McKee-1
Mc-2	McKee-2
Mc-3A	McKee-3A
Mo	Moki-1
Mot	Moturoa
P-1	Pouri-1, McKee Field
R-1	Republic-1
R-4	Republic-4
T-5	Taranaki-5
T-1	Tuhua-1, McKee Field
U	Urenui-1
WaS	Waitangi Seep
WS	Waiotapu Seep

Figure 28: Plot of API gravity versus Ni+V concentration (µg/g) for some New Zealand oils

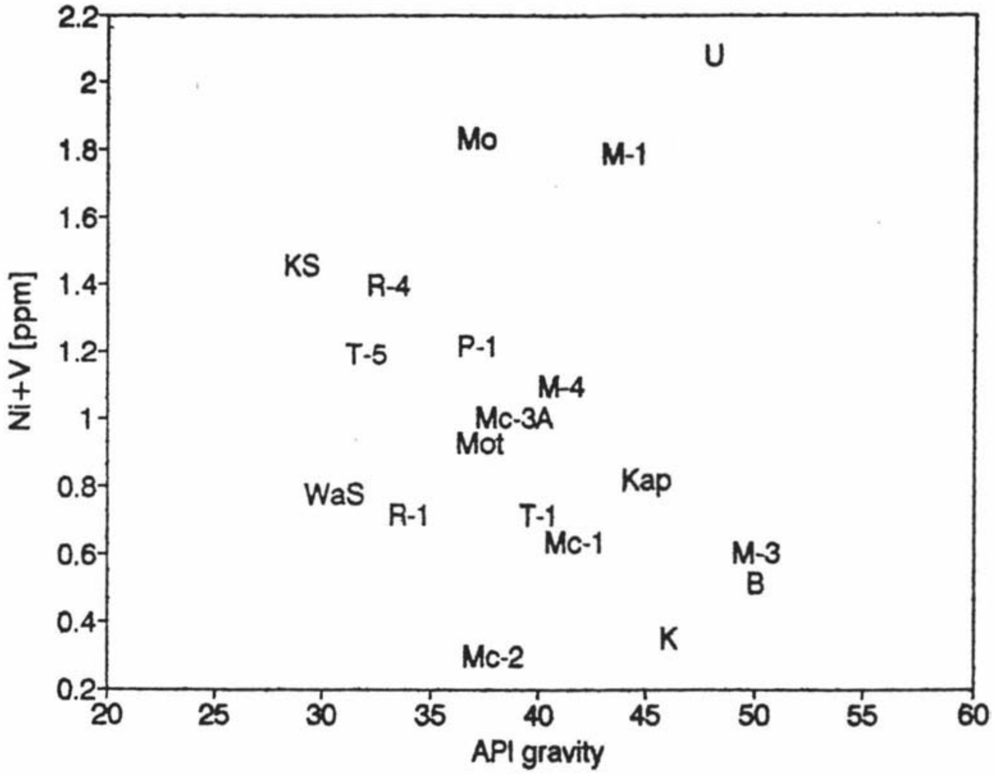
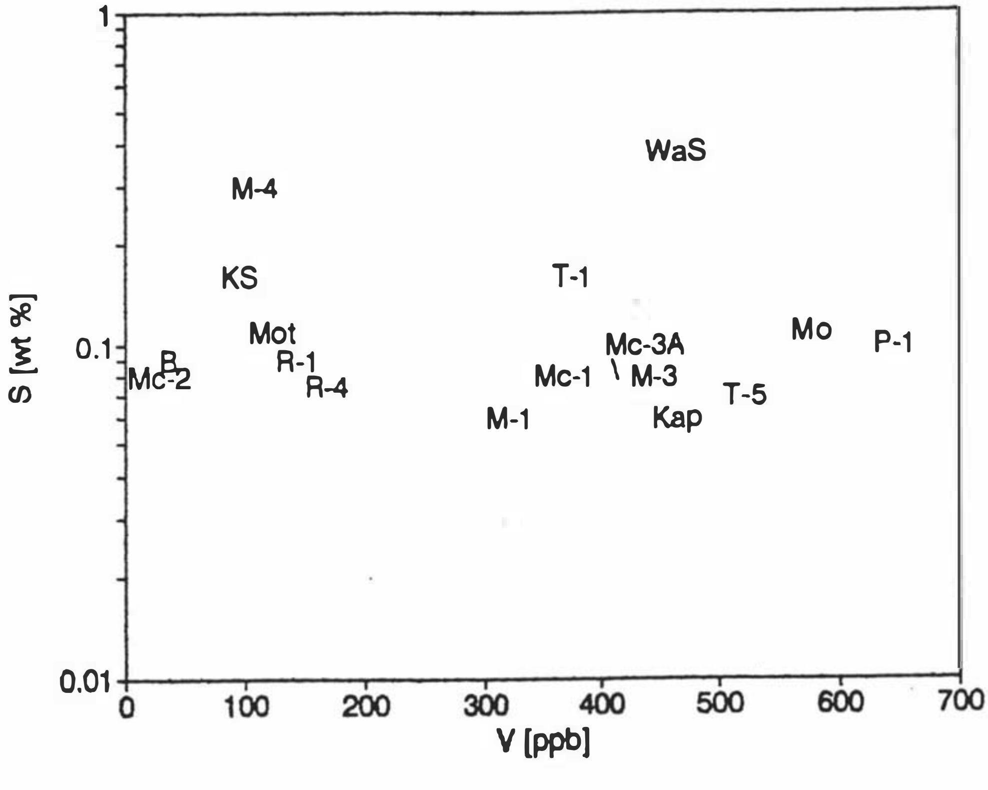


Figure 29: Plot of S (wt %) versus V (ng/g) for New Zealand oils



Nickel and V alone cannot help to shed any light on relationship, migration or source rock differences of oils from the Taranaki Basin, as both concentrations are extremely low and very variable within one field. The ratios and V values, in particular, differ greatly in oils produced from the same field. Oils with marine influence and samples from other areas in New Zealand are not distinguishable by their V or Ni concentrations or ratios.

4.1.2 Bromine and Chlorine

Bromine and Cl are two elements found in the relatively high concentrations of 6.7×10^4 µg/L and 1.9×10^7 µg/L in seawater (*Mason* and *Moore 1982)* and could be useful as indicators of marine influence.

The average concentrations of Br and Cl in New Zealand oils are 187 ng/g and 36.1 µg/g respectively. The high content in some oils might be due to saline water dispersed in the oil, although not all oils high in Br also contain large amounts of Cl. The Moturoa-1 oil has the highest Br and Cl concentrations of 1900 ng/g and 403 µg/g. The Ahuroa-2 condensate has the lowest Br content (1.6 ng/g) and the lowest Cl concentration (7.22 µg/g) can be found in the ToeToe-3 oil.

Neither the Br nor the Cl content varies with the degree of marine influence, as not all oils with marine influence contain higher concentrations of these two elements. The Waitangi Seep, Maui-1 and Moki-1 oils have Br and Cl values above the average content, but the two Kora-1 oil samples contain less Br and Cl than some McKee oils.

4.1.3 Aluminium

The Al concentrations in New Zealand oils vary widely from 1.32 to 208 µg/g with an average concentration of 34.5 µg/g. Maui-1, Moki-1, Waitangi Seep and Taranaki-5 contain the highest amounts of the element. Aluminium and Na are the two elements found in the highest average concentrations in New Zealand crude oils. The Al content in oils is very little affected by filtration, but small particles of clay in the oil, possibly even bound to the polar fractions, might not be affected by filtration and could be, at least partially, responsible for the high Al content in some oils.

4.1.4 Chalcophile elements: Cu, Zn, As, Se, Sb, Pb, Cd

Arsenic is associated with geothermal activity and the concentration of this element in the Waiotapu Seep oil is extremely high. The As concentration is about 10000 times above the average content in other New Zealand oils. The As content (10 µg/g) in the Kotuku Seep oil is also very high when compared to other oil samples. All other New Zealand oils show only small variations in their As concentrations with an average content of 29.5 ng/g. High As contents are not common in all seep oils, as the Waitangi oil contains only 0.11 µg/g, slightly higher than in other crude oils, but far below the amount of the two other seep oil samples.

The concentrations of Cd, Cu, Pb and Sb show only small variations amongst the different oils, with average values in the ng/g range for all these elements. The Taranaki-5 oil has a high Cd concentration of 1.05 µg/g, about 10 times as much as the average for all other oils. Moki-1, Republic-1 and Republic-4 contain the highest amounts of Cu and Pb. Maui-1 and Pukearuhe-1 differ from other oils in their Sb content.

The Zn values for most New Zealand oils are in the ng/g range. Only Kora-1, Moturoa-1, Pukearuhe, Kupe-3, Republic-1 and Republic-4 oil samples contain µg/g amounts of Zn, with both Kora-1 samples showing the highest concentrations of this element, about 20 times higher than in most other samples. None of the seep oils shows any distinct high concentrations and they are not distinguishable from other crude oils by their content of Cd, Cu, Pb or Zn. The Se concentrations were below the detection limit for most oils.

None of these elements by itself allows for a definite discrimination between oils from separate fields. Several of the above elements show distinct differences in concentrations in some individual oils, but vary only slightly in other oils and are not useful in identifying any related oils or specific groups.

4.1.5 Siderophile elements: Fe, Co, Mo, Cr, Mn

The Fe concentrations in New Zealand oils are relatively high with an average content of 24.7 µg/g. The highest Fe content can be found in the Waitangi seep oil and the Moturoa-1 oil. Condensates and oils from the ToeToe wells contain very little Fe with concentrations below 10 µg/g. The amount of Fe in oils is about 100 times higher than the Mn concentrations and about 500 times higher than the average Co concentrations in oil. Contamination by well equipment and pipes is possible, although filtration did not affect the values.

The Co concentrations range from 2.9-326.0 ng/g with an average of 44.5 ng/g. The Co contents in Maui-1, Maui-4, Kora-1, Kotuku Seep and Pukearuhe-1 oils are high compared to all other oils, which have Co contents below the average value. The Co content in the Waitangi seep oil is extremely low and lies in the range of Co concentrations in condensates.

The oils contain only very little Cr and Mn, with an average concentration of 196 ng/g and 264 ng/g respectively. Both elements occur only in small quantities in condensate samples, but high amounts of Mn are found in the Pukearuhe-1, Kotuku and Waitangi seep oils and in samples produced from shallow reservoirs, Moturoa, Republic-4 and Taranaki-5 oils. Chromium values vary only slightly between different samples and none of the oils showed any distinctive high amounts.

The Mo concentrations in Taranaki oils were mostly below the detection limit. Pukearuhe-1 contains 2570 ng/g Mo, a concentration 10 times higher than the average value in other oils that contained detectable amounts. The Mo values in other oils with measurable concentrations range from 64-623 ng/g.

4.1.6 Rare Earth Elements: Eu, La, Sc, Sm

The content of rare earth elements lies in the ng/g range for all analysed oils, with only small variations between different samples. Most rare earth elements, such as Hf, Gd, Tb, Th and U, had concentrations below the detection limit of INAA in most samples.

4.1.7 Inter-elemental correlations

The trace element concentrations were evaluated by correlation analysis to gain information about associations of elements and to study the relationships between them. The correlation matrix obtained by statistical treatment of a set of data is a measure of the similarity of information contained in 2 variables. The correlation coefficient r is an indicator of the degree of association between two sets of variables. If r equals 1, x varies in perfect unison with y. A r-value of 0 indicates that no linear correlation exists.

The element concentrations in New Zealand oils are log- normally distributed, as the median of individual element concentrations equals the geometric mean[1]. Correlation analysis was performed using log values of the original data and the results of the statistical analysis are listed in Figure 30. Whether or not the correlation is statistically significant, depends on the probability value, which in turn is a function of the correlation coefficient r and the number of samples. Figure 30 is a table showing significances, calculated from P. The original correlation matrix, mean and standard deviation values are listed in Appendix K.

The highest mutual correlations were found for Al, Cr, Fe, Mn, Na, Sc, Sm and V. Graphs, e.g. Al versus V (Figure 31) show an almost linear relationship between these highly correlated elements. All these elements are strongly associated with clay minerals, which are formed by decomposition of aluminosilicates.

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[1] $\sqrt[n]{x_1,x_2,\ldots,x_n}$ *or antilog*$[\frac{\Sigma \log x_n}{n}]$ *with n number of samples*

These mutually high correlations point to a common origin of these elements and they either could be derived from the original organic source rocks, or could have been picked up as clay particles during migration. In clays, Al can be replaced by Fe, Zn, Cr and Mn, and other elements, e.g. Sc and Sm, get complexed in the layers of clay minerals. The grain sizes of clays are usually very small with a maximum dimension of 2 microns, and can range down to colloidal dimensions, resulting in a gel-like appearance (*Mason* and *Moore 1984)*. Kaolinite is a clay mineral common in terrestrial sediments and is present as small particles in rock pores in many Cretaceous and Lower Tertiary sediments of Taranaki Basin. Its grain size allows it to pass through existing pore space in the rocks during fluid movement (*Collen, pers. comm.)*. Kaolinite is a two layer clay mineral and its formation is favoured in an acid environment (*Mason* and *Moore 1984)*. In comparison, illite, a form of clay most common in marine sediments, tends to attach to existing rock particles, making it less mobile than kaolinite.

It is likely that clay particles picked up by the oils during migration or in the reservoir contribute a great deal to the total trace element concentrations in the oil. As the clay minerals can occur very finely dispersed, filtration or centrifugation would not have a large effect.

The presence of mineral matter in the oils and their effect on the element content, especially V, could also explain why this element concentration and the Ni/V or V/Ni ratios vary strongly and why their values are not useful in identifying related oils and groups Figure 31a). All other geochemical studies suggested that the oils in the Taranaki Basin are closely related (*Czochanska et al. 1988)* and the presence of finely dispersed minerals contributing to the total trace element content could help to explain why trace element variations in related oils are larger than analytical or sampling errors. The small variations of elements associated mainly with organic fractions in related oils (e.g. Ni and Co) and not clay, could indicate that the oils from the same fields are very similar and that the observed differences are due to matter that is not bound organically and has been introduced during migration or in the reservoir.

Figure 30: Correlation matrix for New Zealand oils

New Zealand oils, inter-elemental correlations

	Al	As	Br	Cl	Co	Cr	Cs	Eu	Fe	Mn	Na	Ni	Sb	Sc	Sm	V	Zn
Al		NS	S^{*}	NS	S	S^{**}	S	S^{*}	S^{**}	S^{**}	S^{**}	NS	S^{**}	S^{**}	S^{**}	S^{**}	N S
As			NS	NS	S	NS	NS	NS	S	S^{*}	NS	S	NS	NS	NS	NS	S
Br				S^{**}	NS	S	NS	NS	S^{**}	S^{*}	S^{**}	S^{**}	NS	S^{*}	S^{*}	S	S
Cl					NS	NS	NS	NS	S^{*}	NS	S^{*}	S^{**}	NS	NS	NS	NS	S
Co						S^{*}	NS	NS	S^{**}	S^{**}	S^{*}	S^{**}	S	NS	S	S	S^{**}
Cr							S	S	S^{**}	S^{**}	S^{**}	NS	S^{**}	S^{**}	S^{**}	S^{**}	NS
Cs								S^{*}	NS	NS	NS	NS	S	S	NS	NS	S
Eu									S	NS	NS	NS	S^{*}	S^{*}	S^{*}	S	NS
Fe										S^{**}	S^{**}	S^{*}	S^{**}	S^{**}	S^{**}	S^{**}	S
Mn											S^{*}	S^{**}	S^{*}	S^{**}	S^{**}	S^{**}	S^{**}
Na												NS	S^{*}	S^{**}	S^{*}	S^{**}	NS
Ni													S	NS	NS	S	S^{**}
Sb														S^{**}	S^{**}	S^{*}	NS
Sc															S^{**}	S^{**}	NS
Sm																S^{**}	NS
V																	NS

S^{**} very highly significant, $r > 0.465$ ($P < 0.001$)

S^{*} highly significant, $0.372 < r \leq 0.465$ ($0.001 \leq P < 0.01$)

S significant, $0.287 < r \leq 0.372$ ($0.01 \leq P < 0.05$)

LEGEND

1	Ahuroa-2
2	Blackwater
3	Galleon-1
4	Kaimiro-1
5	Kapuni-1
6	Kora-1, DST2
7	Kora-1, DST3
8	Kotuku Seep
9	Kupe South
10	Kupe-2
11	Kupe-3
12	Kupe-4
13	Kupe-5
14	Maui-1
15	Maui-3
16	Maui-4
17	McKee-1
18	McKee-2
19	McKee-3A
20	McKee-4
21	Moki-1
22	Moturoa
23	Pouri-1
24	Pukearuhe-1
25	Pukemai-1B
26	Pukemai-2
27	Republic-1
28	Republic-4
29	Stratford-1
30	Stratford-1
31	Taranaki-5
32	Tariki-1
33	Tariki-1A
34	ToeToe-1
35	ToeToe-2B
36	ToeToe-3
37	ToeToe-4
38	Toru-1
39	Tuhua-1
40	Tuhua-2
41	Tuhua-2, A-Sand
42	Tuhua-2, B-Sand
43	Urenui-1
44	Waihapa
45	Waiotapu Seep
46	Waitangi Seep

Well	
McKee-1	Mc-1
McKee-2	Mc-2
McKee-3A	Mc-3A
McKee-4	Mc-4
Pouri-1	P-1
Pukemai-1B	P-1B
Pukemai-2	P-2
ToeToe-1	TT-1
ToeToe-2B	TT-2B
ToeToe-3	TT-3
ToeToe-4	TT-4
Tuhua-1	T-1
Tuhua-2	T-2
Tuhua-2, A-Sand	T-2
Tuhua-2, B-Sand	T-2

Figure 31: Aluminium (µg/g) versus V (ng/g) for New Zealand oils

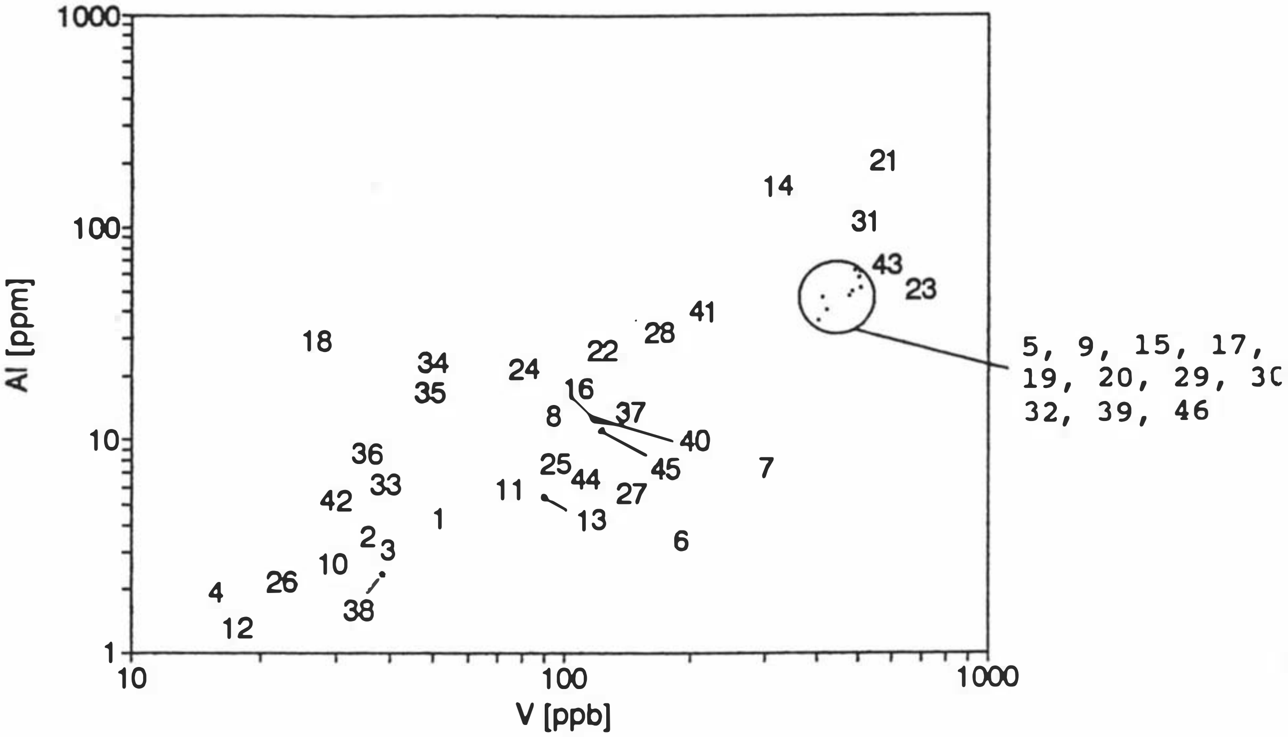
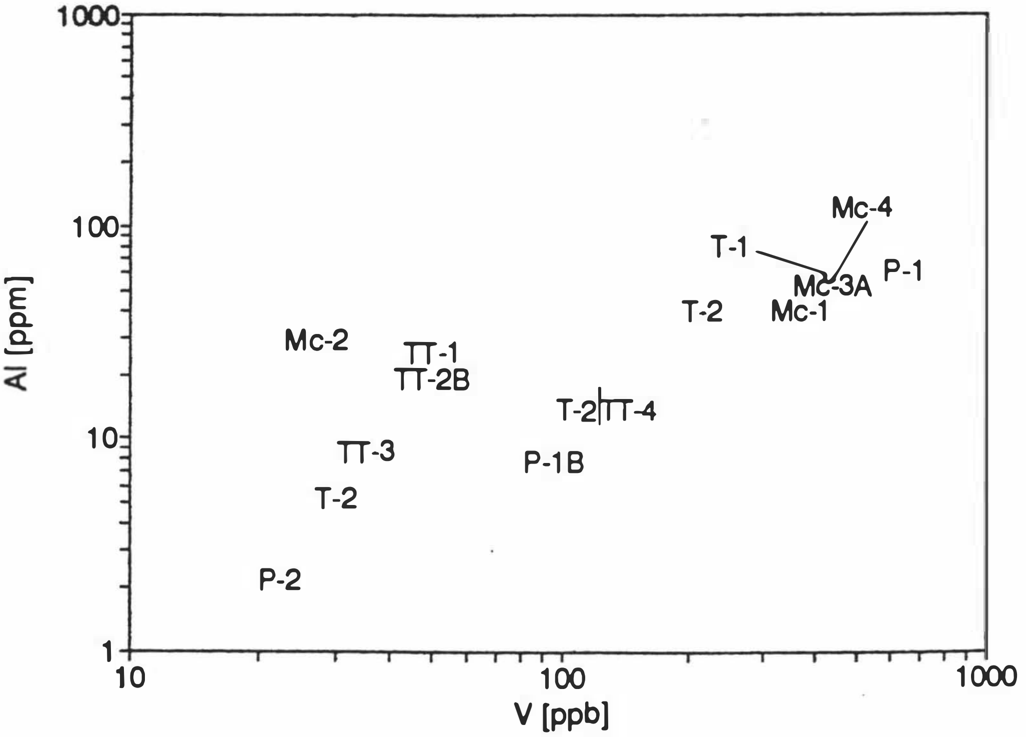


Figure 31a: Aluminium (µg/g) and V (ng/g) in oils from the McKee Field



It is also possible that certain elements present in the oils are partially derived from the original organic matter, as *Goldschmidt (1954)* reported that certain tree ferns accumulate Al and that coal measure plants might have been Al accumulators. This possibility is supported by the high Al:Si ratio found in certain coal ashes that cannot be only due to contamination by minerals. *Newman (1987)* showed that certain coals from the West Coast of New Zealand contain high concentrations of Al, partly in the form of γ-AlO[OH] (boehmite), which points to an unusual depositional environment.

The siderophile elements Co, Fe, Mn and Ni also show very highly significant correlation coefficients. A graph of Co versus Mn (Figure 33) clearly separates the Maui-1, Maui-4, Pukearuhe-1, Kora-1 oils and the Kotuku seep oil from other New Zealand oils, although the separation is not as clear in plots with logarithmic scale (Figure 32). Oils produced from shallow reservoirs (Moturoa, Taranaki-5 and Republic-4) contain low amounts of Co, but differ slightly from other oils in their Mn concentrations.

Bromine, Cl and Na, elements found in saline waters, show high mutual correlations, but their plots do not allow the subdivision of oils. Graphs of other correlated elements do not allow for discrimination of different groups, although in most plots the oils from the Maui field, Kora-1 oil samples, Pukearuhe-1 and seep oil samples are usually slightly separate. Most condensates lie in the lower concentration ranges, whereas McKee oils are distributed evenly throughout graphs. An Fe versus Sc plot singles out the Taranaki-5, Moturoa and Waitangi Seep oil with all other oils distributed in two separate clusters (Figure 34). The Co/As and Ni/As (Figure 35 and 36) graphs separate the Kotuku, Waiotapu and Waitangi Seep oils, as well as the Kora and Maui-1 samples, from the rest of the oils. Arsenic is relatively evenly distributed in all oils, with only Kotuku Seep and Waiotapu Seep oils containing distinctly high amounts of this element. None of the other graphs of correlated elements, like Ni/Zn (Figure 37) or uncorrelated elements, like As/Br (Figure 38) supplied any different information. The oils are distributed more or less randomly in the plots and only slight separation of Kora, Pukearuhe and Maui oils is obvious in some of the graphs. Oil samples from Taranaki Basin are not distinguishable into individual groups of related hydrocarbons based on graphs of correlated or uncorrelated elements. Even oils from one oilfield show large variations in their trace element content, as is shown in some of the graphs for oils of the McKee Field.

The oils could be closely related and their trace element contents have been altered by contamination or migration (loss of polar components), resulting in large variations of trace element content. The second possibility is that the oils have been derived from different source rocks and subsequent migration or contamination effects have obscured individual groups of different oils. However, it is not possible to come to a definite conclusion based on the data available.

LEGEND

1	Ahuroa-2	24	Pukearuhe-1
2	Blackwater	25	Pukemai-1B
3	Galleon-1	26	Pukemai-2
4	Kaimiro-1	27	Republic-1
5	Kapuni-1	28	Republic-4
6	Kora-1, DST2	29	Stratford-1
7	Kora-1, DST3	30	Stratford-1
8	Kotuku Seep	31	Taranaki-5
9	Kupe South	32	Tariki-1
10	Kupe-2	33	Tariki-1A
11	Kupe-3	34	ToeToe-1
12	Kupe-4	35	ToeToe-2B
13	Kupe-5	36	ToeToe-3
14	Maui-1	37	ToeToe-4
15	Maui-3	38	Toru-1
16	Maui-4	39	Tuhua-1
17	McKee-1	40	Tuhua-2
18	McKee-2	41	Tuhua-2, A-Sand
19	McKee-3A	42	Tuhua-2, B-Sand
20	McKee-4	43	Urenui-1
21	Moki-1	44	Waihapa
22	Moturoa	45	Waiotapu Seep
23	Pouri-1	46	Waitangi Seep

<u>Well</u>	
McKee-1	Mc-1
McKee-2	Mc-2
McKee-3A	Mc-3A
McKee-4	Mc-4
Pouri-1	P-1
Pukemai-1B	P-1B
Pukemai-2	P-2
ToeToe-1	TT-1
ToeToe-2B	TT-2B
ToeToe-3	TT-3
ToeToe-4	TT-4
Tuhua-1	T-1
Tuhua-2	T-2
Tuhua-2, A-Sand	T-2
Tuhua-2, B-Sand	T-2

Figure 32: Cobalt (ng/g) versus Mn (ng/g) for New Zealand oils

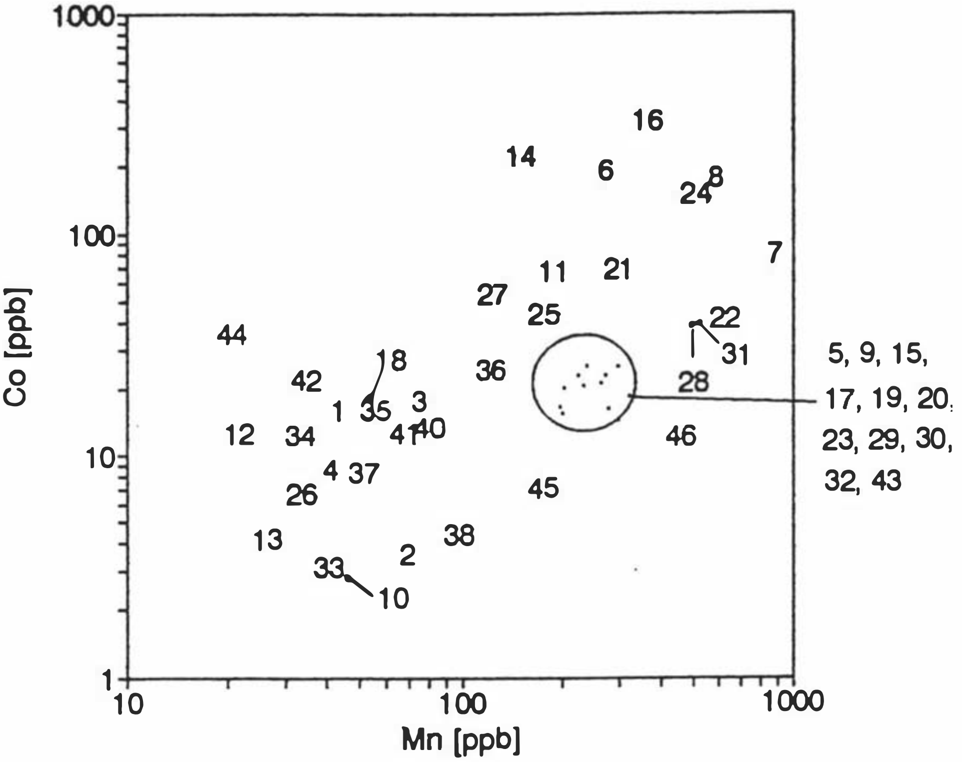


Figure 32a: Cobalt (ng/g) and Mn (ng/g) in oils from the McKee Field

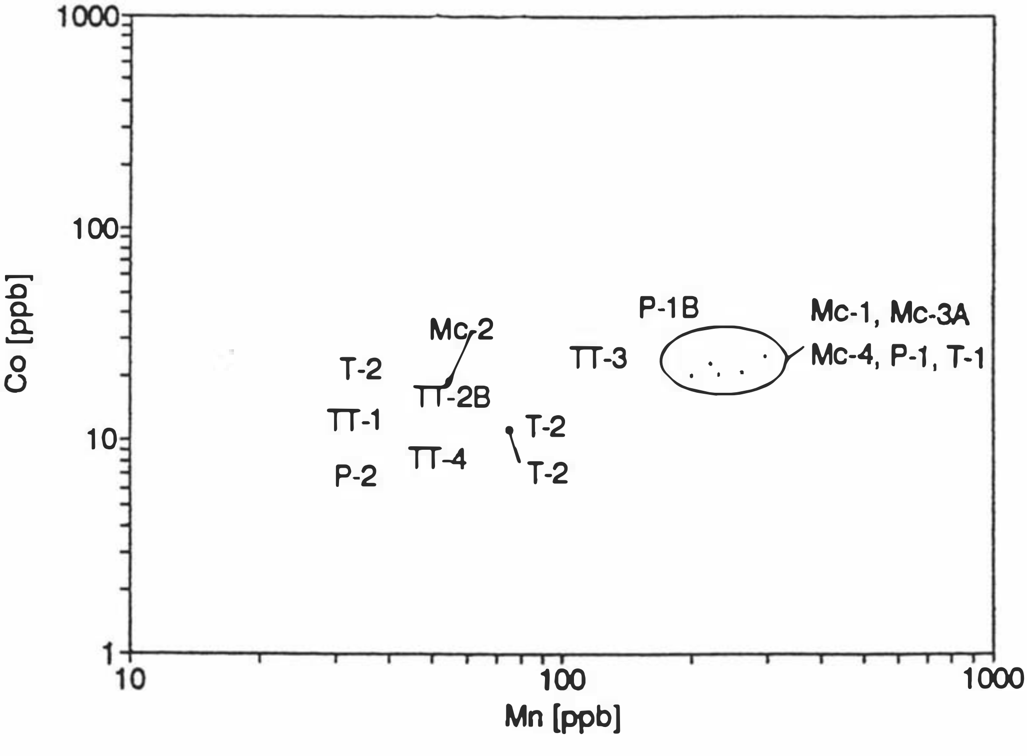
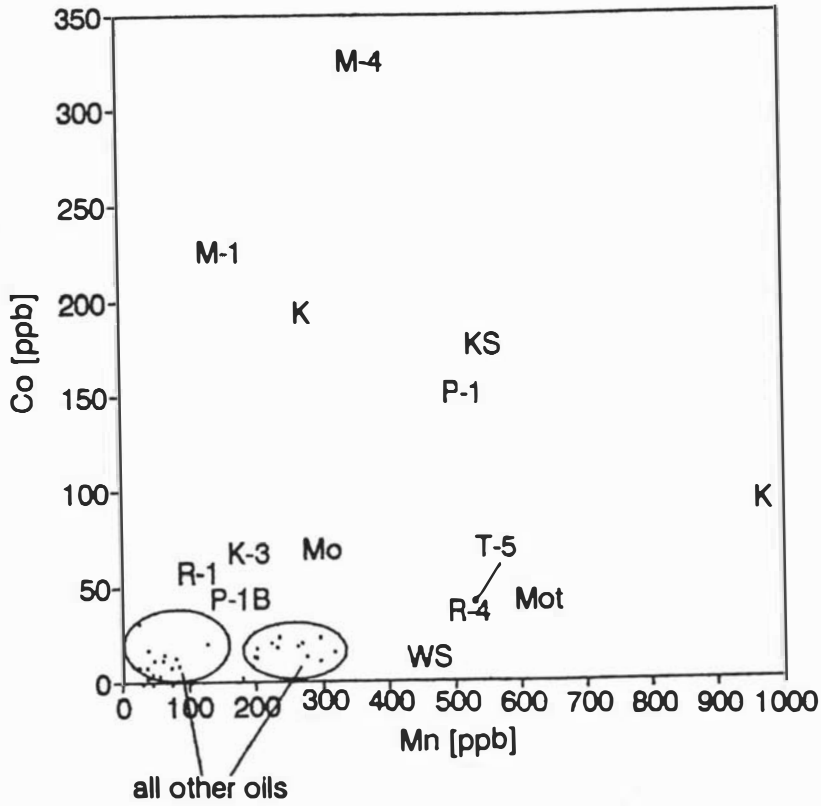


Figure 33: Cobalt (ng/g) versus Mn (ng/g) (normal scale)



Well	
Kora-1, DST2	K
Kora-1, DST3	K
Kotuku Seep	KS
Kupe-3	K-3
Maui-1	M-1
Maui-4	M-4
Moki-1	Mo
Moturoa	Mot
Pukearuhe-1	P-1
Pukemai-1B	P-1B
Republic-1	R-1
Republic-4	R-4
Taranaki-5	T-5

LEGEND

1	Ahuroa-2	24	Pukearuhe-1
2	Blackwater	25	Pukemai-1B
3	Galleon-1	26	Pukemai-2
4	Kaimiro-1	27	Republic-1
5	Kapuni-1	28	Republic-4
6	Kora-1, DST2	29	Stratford-1
7	Kora-1, DST3	30	Stratford-1
8	Kotuku Seep	31	Taranaki-5
9	Kupe South	32	Tariki-1
10	Kupe-2	33	Tariki-1A
11	Kupe-3	34	ToeToe-1
12	Kupe-4	35	ToeToe-2B
13	Kupe-5	36	ToeToe-3
14	Maui-1	37	ToeToe-4
15	Maui-3	38	Toru-1
16	Maui-4	39	Tuhua-1
17	McKee-1	40	Tuhua-2
18	McKee-2	41	Tuhua-2, A-Sand
19	McKee-3A	42	Tuhua-2, B-Sand
20	McKee-4	43	Urenui-1
21	Moki-1	44	Waihapa
22	Moturoa	45	Waiotapu Seep
23	Pouri-1	46	Waitangi Seep

<u>Well</u>	
McKee-1	Mc-1
McKee-2	Mc-2
McKee-3A	Mc-3A
McKee-4	Mc-4
Pouri-1	P-1
Pukemai-1B	P-1B
Pukemai-2	P-2
ToeToe-1	TT-1
ToeToe-2B	TT-2B
ToeToe-3	TT-3
ToeToe-4	TT-4
Tuhua-1	T-1
Tuhua-2	T-2
Tuhua-2, A-Sand	T-2
Tuhua-2, B-Sand	T-2

Figure 34: Iron (µg/g) versus Sc (ng/g) for New Zealand oils

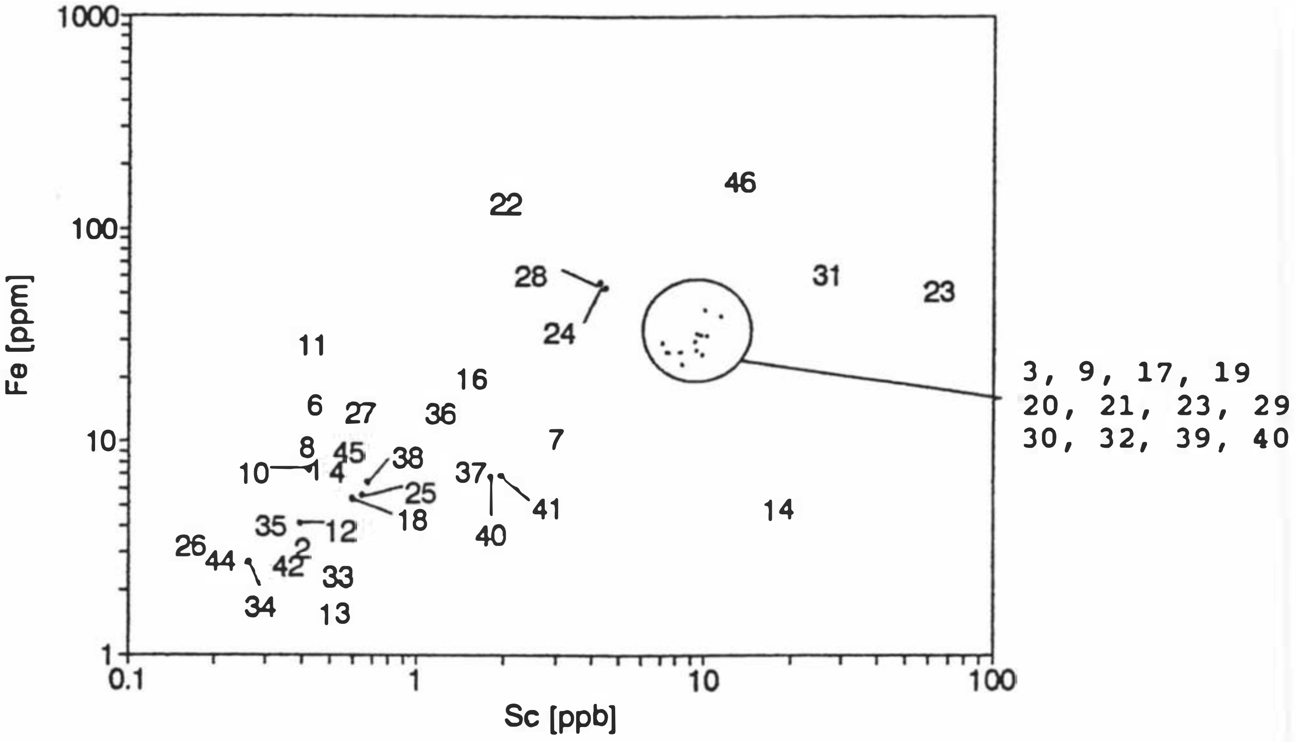
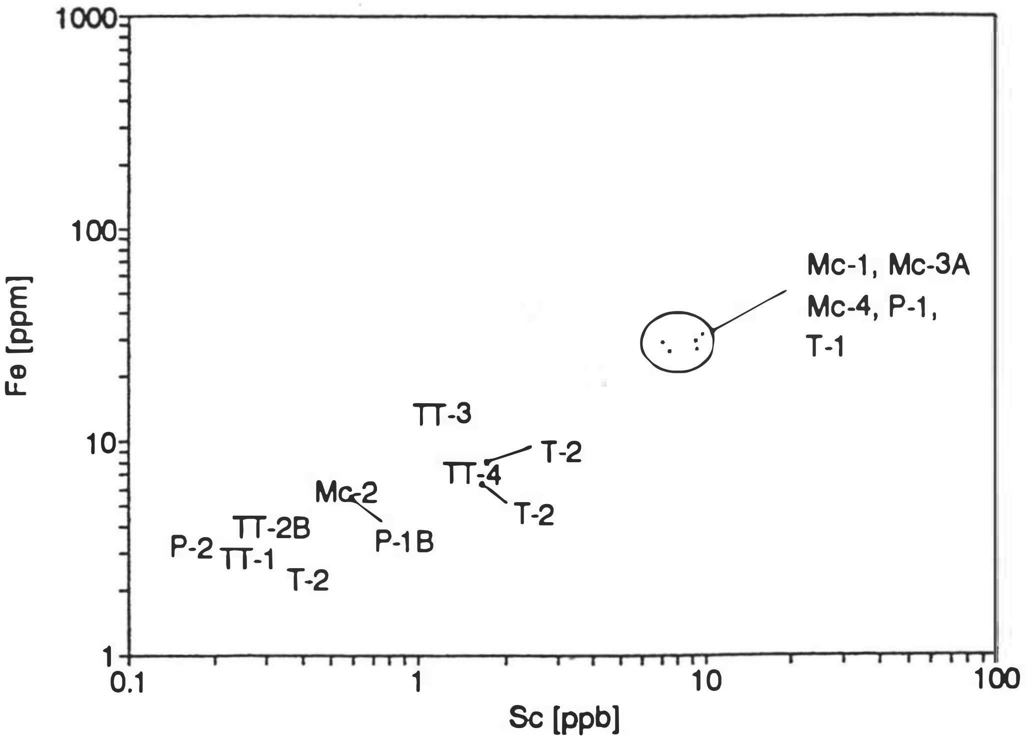


Figure 34a: Iron (µg/g) and Sc (ng/g) in oils from the McKee Field



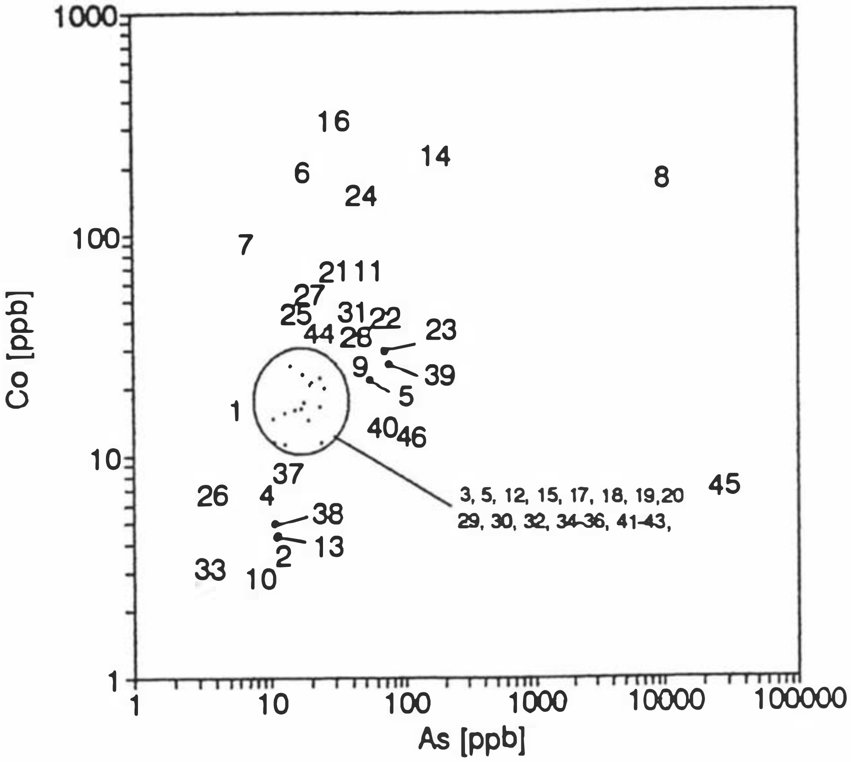
LEGEND

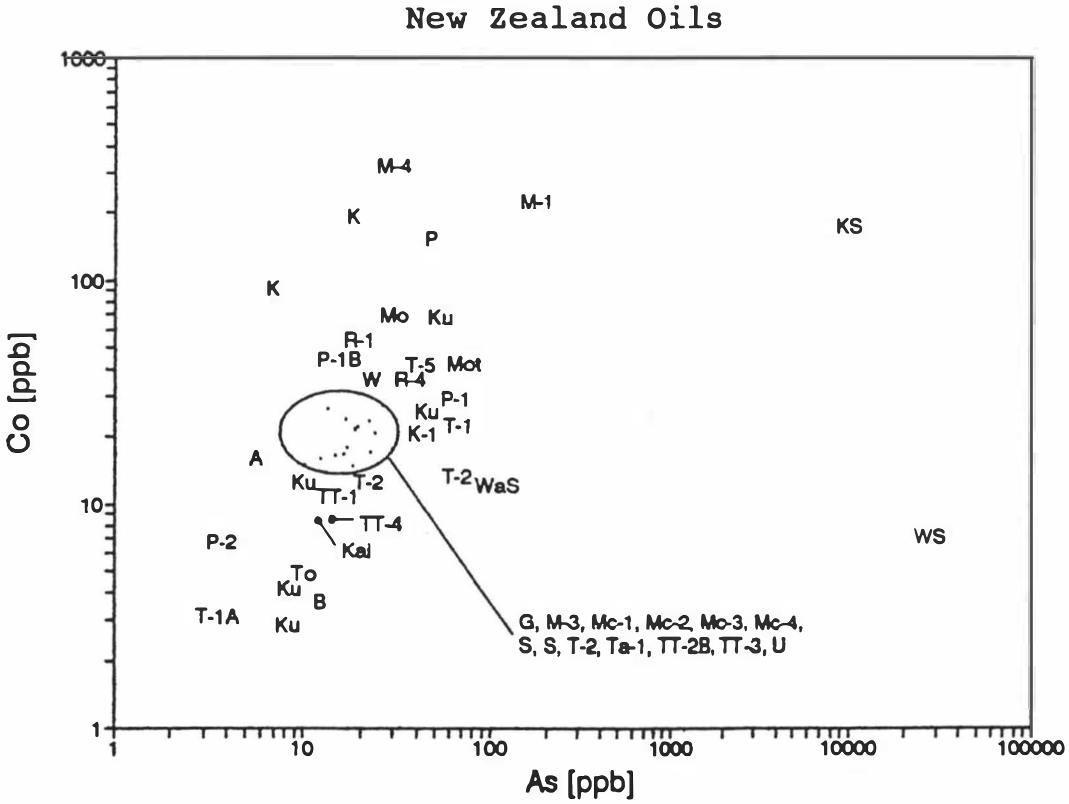
1	Ahuroa-2	24	Pukearuhe-1
2	Blackwater	25	Pukemai-1B
3	Galleon-1	26	Pukemai-2
4	Kaimiro-1	27	Republic-1
5	Kapuni-1	28	Republic-4
6	Kora-1, DST2	29	Stratford-1
7	Kora-1, DST3	30	Stratford-1
8	Kotuku Seep	31	Taranaki-5
9	Kupe South	32	Tariki-1
10	Kupe-2	33	Tariki-1A
11	Kupe-3	34	ToeToe-1
12	Kupe-4	35	ToeToe-2B
13	Kupe-5	36	ToeToe-3
14	Maui-1	37	ToeToe-4
15	Maui-3	38	Toru-1
16	Maui-4	39	Tuhua-1
17	McKee-1	40	Tuhua-2
18	McKee-2	41	Tuhua-2, A-Sand
19	McKee-3A	42	Tuhua-2, B-Sand
20	McKee-4	43	Urenui-1
21	Moki-1	44	Waihapa
22	Moturoa	45	Waiotapu Seep
23	Pouri-1	46	Waitangi Seep

LEGEND

A	Ahuroa-2	P	Pukearuhe-1
B	Blackwater	P-1B	Pukemai-1B
G	Galleon-1	P-2	Pukemai-2
Kai	Kaimiro-1	R-1	Republic-1
K-1	Kapuni-1	R-4	Republic-4
K	Kora-1, DST2	S	Stratford-1
K	Kora-1, DST3	S	Stratford-1
KS	Kotuku Seep	T-5	Taranaki-5
Ku	Kupe South	Ta-1	Tariki-1
Ku	Kupe-2	T-1A	Tariki-1A
Ku	Kupe-3	TT-1	ToeToe-1
Ku	Kupe-4	TT-2B	ToeToe-2B
Ku	Kupe-5	TT-3	ToeToe-3
M-1	Maui-1	TT-4	ToeToe-4
M-3	Maui-3	To	Toru-1
M-4	Maui-4	T-1	Tuhua-1
Mc-1	McKee-1	T-2	Tuhua-2
Mc-2	McKee-2	T-2	Tuhua-2, A-Sand
Mc-3	McKee-3A	T-2	Tuhua-2, B-Sand
Mc-4	McKee-4	U	Urenui-1
Mo	Moki-1	W	Waihapa
Mot	Moturoa	WS	Waiotapu Seep
P-1	Pouri-1	WaS	Waitangi Seep

Figure 35: Cobalt (ng/g) versus As (ng/g)





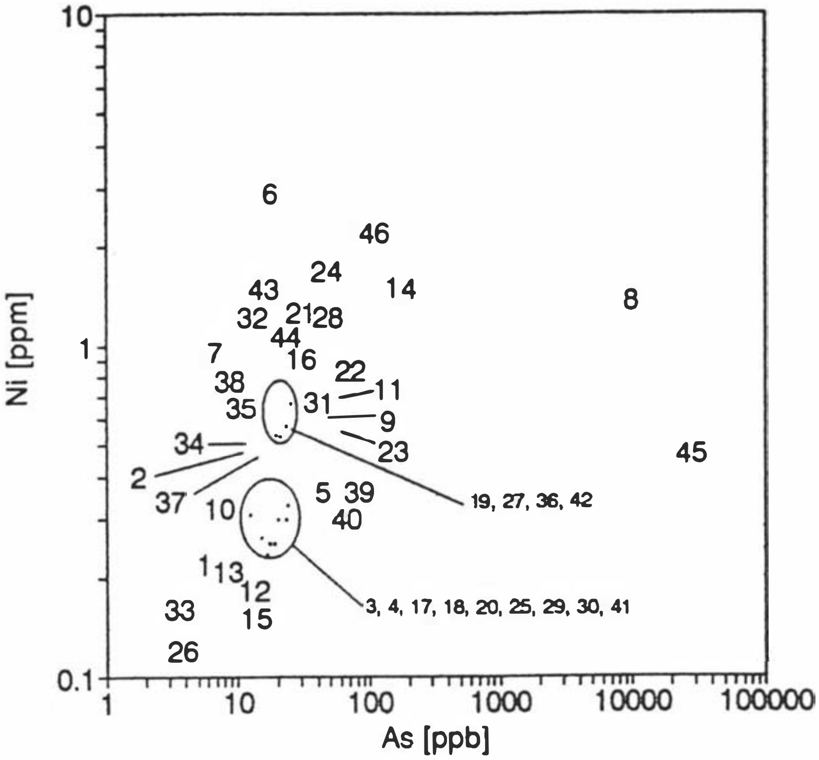
LEGEND

1	Ahuroa-2	24	Pukearuhe-1
2	Blackwater	25	Pukemai-1B
3	Galleon-1	26	Pukemai-2
4	Kaimiro-1	27	Republic-1
5	Kapuni-1	28	Republic-4
6	Kora-1, DST2	29	Stratford-1
7	Kora-1, DST3	30	Stratford-1
8	Kotuku Seep	31	Taranaki-5
9	Kupe South	32	Tariki-1
10	Kupe-2	33	Tariki-1A
11	Kupe-3	34	ToeToe-1
12	Kupe-4	35	ToeToe-2B
13	Kupe-5	36	ToeToe-3
14	Maui-1	37	ToeToe-4
15	Maui-3	38	Toru-1
16	Maui-4	39	Tuhua-1
17	McKee-1	40	Tuhua-2
18	McKee-2	41	Tuhua-2, A-Sand
19	McKee-3A	42	Tuhua-2, B-Sand
20	McKee-4	43	Urenui-1
21	Moki-1	44	Waihapa
22	Moturoa	45	Waiotapu Seep
23	Pouri-1	46	Waitangi Seep

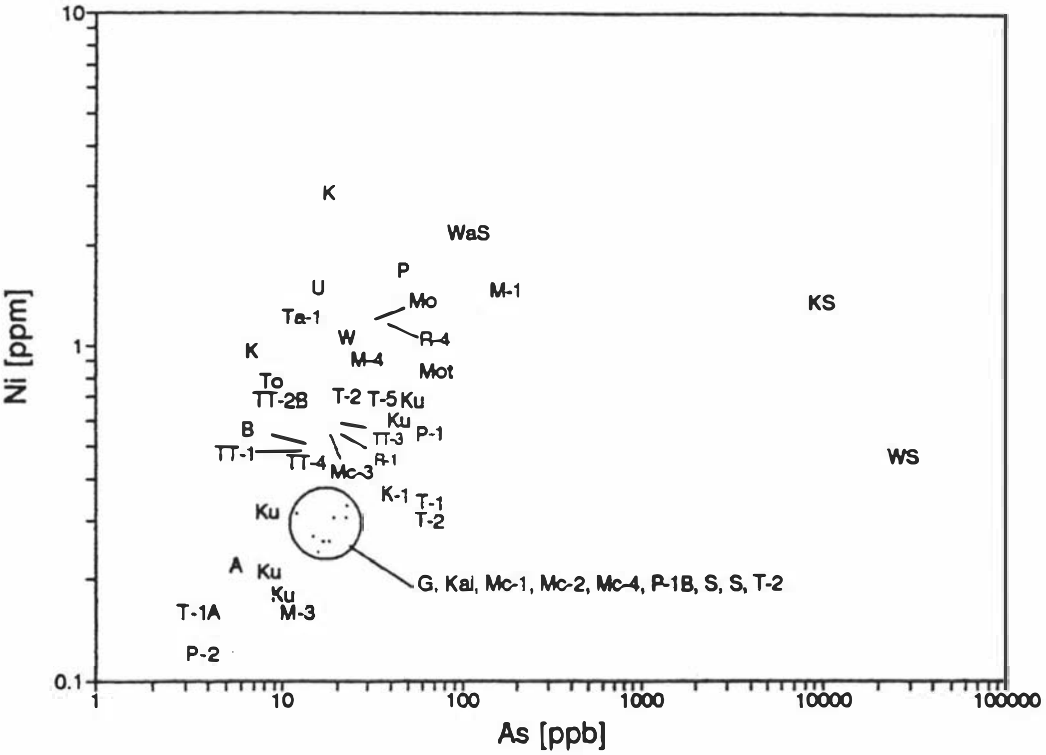
LEGEND

A	Ahuroa-2	P	Pukearuhe-1
B	Blackwater	P-1B	Pukemai-1B
G	Galleon-1	P-2	Pukemai-2
Kai	Kaimiro-1	R-1	Republic-1
K-1	Kapuni-1	R-4	Republic-4
K	Kora-1, DST2	S	Stratford-1
K	Kora-1, DST3	S	Stratford-1
KS	Kotuku Seep	T-5	Taranaki-5
Ku	Kupe South	Ta-1	Tariki-1
Ku	Kupe-2	T-1A	Tariki-1A
Ku	Kupe-3	TT-1	ToeToe-1
Ku	Kupe-4	TT-2B	ToeToe-2B
Ku	Kupe-5	TT-3	ToeToe-3
M-1	Maui-1	TT-4	ToeToe-4
M-3	Maui-3	To	Toru-1
M-4	Maui-4	T-1	Tuhua-1
Mc-1	McKee-1	T-2	Tuhua-2
Mc-2	McKee-2	T-2	Tuhua-2, A-Sand
Mc-3	McKee-3A	T-2	Tuhua-2, B-Sand
Mc-4	McKee-4	U	Urenui-1
Mo	Moki-1	W	Waihapa
Mot	Moturoa	WS	Waiotapu Seep
P-1	Pouri-1	WaS	Waitangi Seep

Figure 36: Nickel (µg/g) versus As (µg/g)



New Zealand Oils



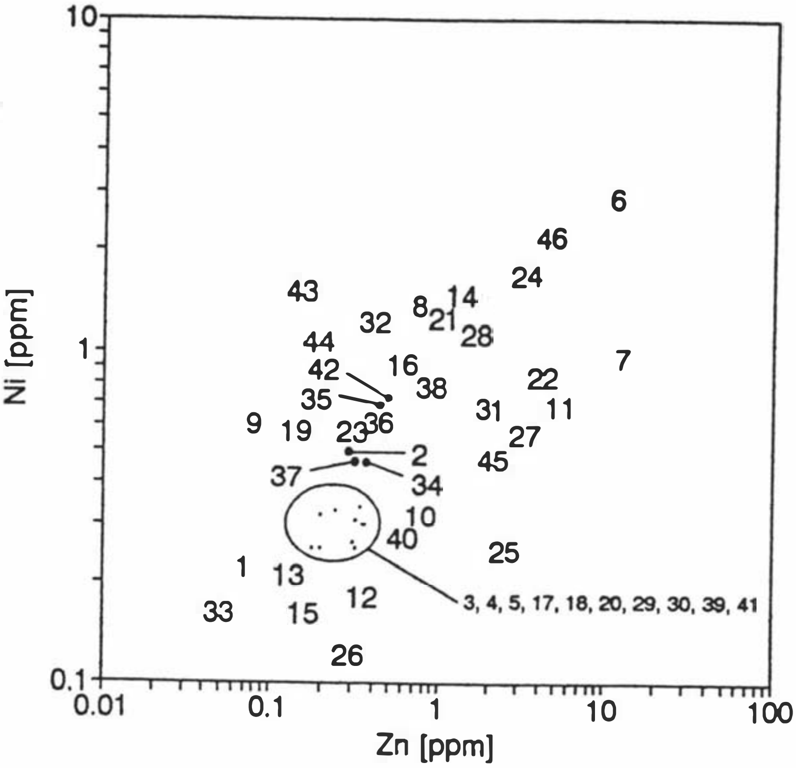
LEGEND

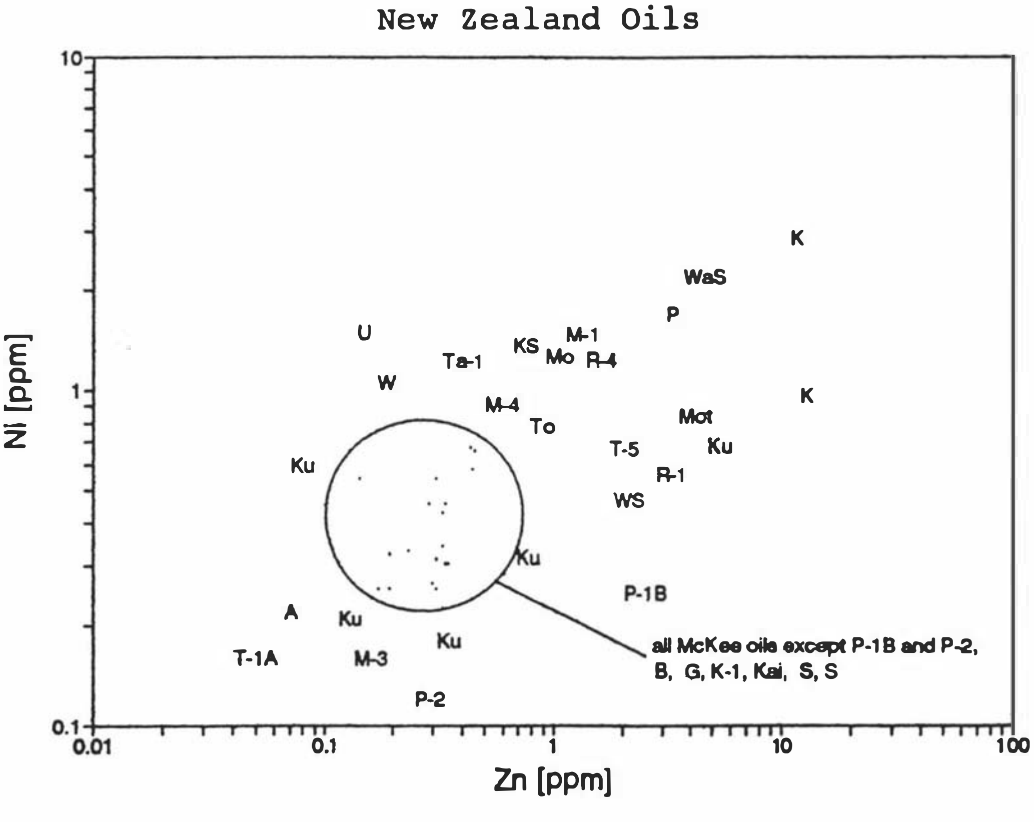
1	Ahuroa-2	24	Pukearuhe-1
2	Blackwater	25	Pukemai-1B
3	Galleon-1	26	Pukemai-2
4	Kaimiro-1	27	Republic-1
5	Kapuni-1	28	Republic-4
6	Kora-1, DST2	29	Stratford-1
7	Kora-1, DST3	30	Stratford-1
8	Kotuku Seep	31	Taranaki-5
9	Kupe South	32	Tariki-1
10	Kupe-2	33	Tariki-1A
11	Kupe-3	34	ToeToe-1
12	Kupe-4	35	ToeToe-2B
13	Kupe-5	36	ToeToe-3
14	Maui-1	37	ToeToe-4
15	Maui-3	38	Toru-1
16	Maui-4	39	Tuhua-1
17	McKee-1	40	Tuhua-2
18	McKee-2	41	Tuhua-2, A-Sand
19	McKee-3A	42	Tuhua-2, B-Sand
20	McKee-4	43	Urenui-1
21	Moki-1	44	Waihapa
22	Moturoa	45	Waiotapu Seep
23	Pouri-1	46	Waitangi Seep

LEGEND

A	Ahuroa-2	P	Pukearuhe-1
B	Blackwater	P-1B	Pukemai-1B
G	Galleon-1	P-2	Pukemai-2
Kai	Kaimiro-1	R-1	Republic-1
K-1	Kapuni-1	R-4	Republic-4
K	Kora-1, DST2	S	Stratford-1
K	Kora-1, DST3	S	Stratford-1
KS	Kotuku Seep	T-5	Taranaki-5
Ku	Kupe South	Ta-1	Tariki-1
Ku	Kupe-2	T-1A	Tariki-1A
Ku	Kupe-3	TT-1	ToeToe-1
Ku	Kupe-4	TT-2B	ToeToe-2B
Ku	Kupe-5	TT-3	ToeToe-3
M-1	Maui-1	TT-4	ToeToe-4
M-3	Maui-3	To	Toru-1
M-4	Maui-4	T-1	Tuhua-1
Mc-1	McKee-1	T-2	Tuhua-2
Mc-2	McKee-2	T-2	Tuhua-2, A-Sand
Mc-3	McKee-3A	T-2	Tuhua-2, B-Sand
Mc-4	McKee-4	U	Urenui-1
Mo	Moki-1	W	Waihapa
Mot	Moturoa	WS	Waiotapu Seep
P-1	Pouri-1	WaS	Waitangi Seep

Figure 37: Nickel (µg/g) versus Zn (µg/g)





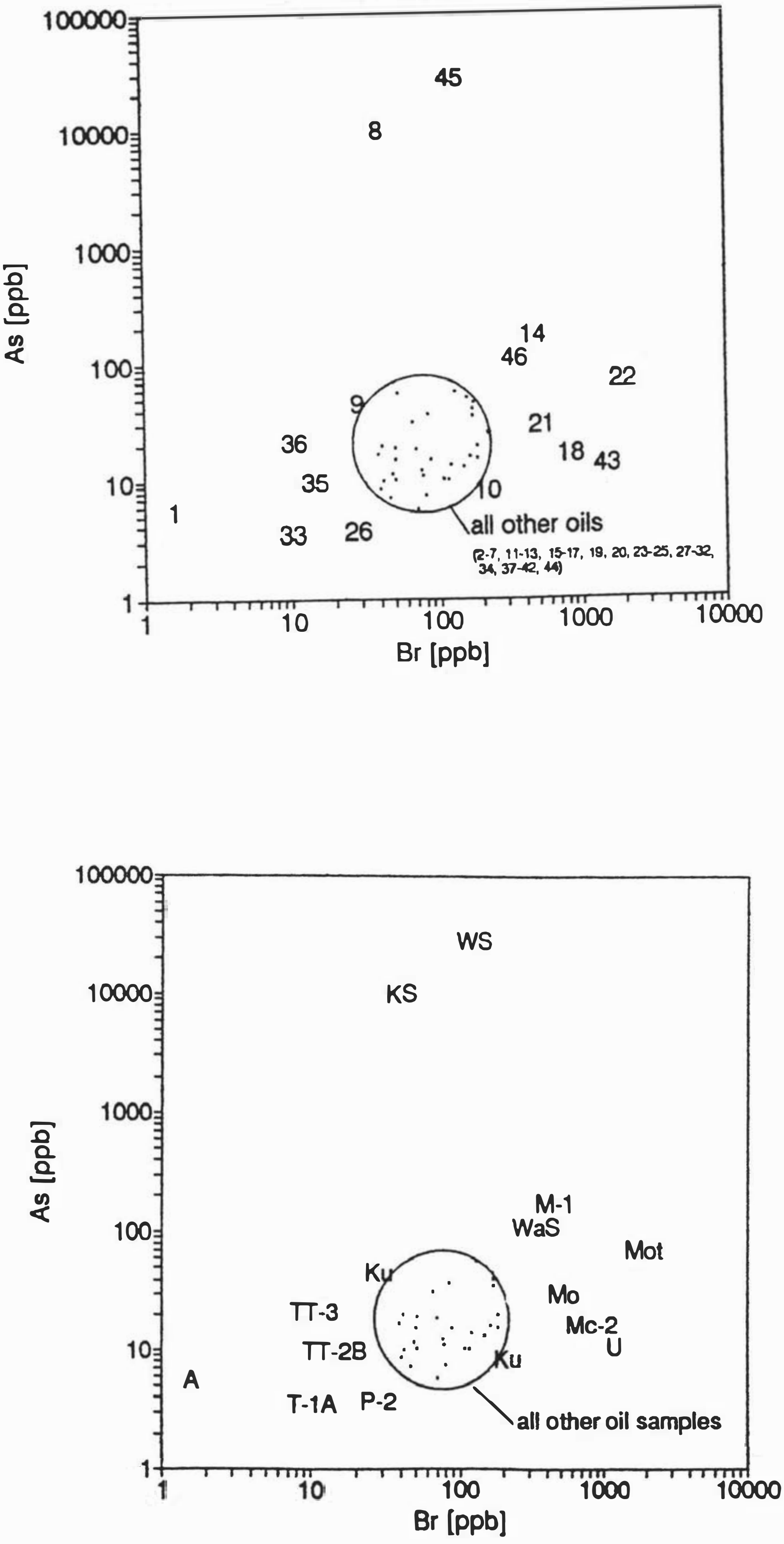
LEGEND

1	Ahuroa-2
2	Blackwater
3	Galleon-1
4	Kaimiro-1
5	Kapuni-1
6	Kora-1, DST2
7	Kora-1, DST3
8	Kotuku Seep
9	Kupe South
10	Kupe-2
11	Kupe-3
12	Kupe-4
13	Kupe-5
14	Maui-1
15	Maui-3
16	Maui-4
17	McKee-1
18	McKee-2
19	McKee-3A
20	McKee-4
21	Moki-1
22	Moturoa
23	Pouri-1
24	Pukearuhe-1
25	Pukemai-1B
26	Pukemai-2
27	Republic-1
28	Republic-4
29	Stratford-1
30	Stratford-1
31	Taranaki-5
32	Tariki-1
33	Tariki-1A
34	ToeToe-1
35	ToeToe-2B
36	ToeToe-3
37	ToeToe-4
38	Toru-1
39	Tuhua-1
40	Tuhua-2
41	Tuhua-2, A-Sand
42	Tuhua-2, B-Sand
43	Urenui-1
44	Waihapa
45	Waiotapu Seep
46	Waitangi Seep

LEGEND

A	Ahuroa-2
B	Blackwater
G	Galleon-1
Kai	Kaimiro-1
K-1	Kapuni-1
K	Kora-1, DST2
K	Kora-1, DST3
KS	Kotuku Seep
Ku	Kupe South
Ku	Kupe-2
Ku	Kupe-3
Ku	Kupe-4
Ku	Kupe-5
M-1	Maui-1
M-3	Maui-3
M-4	Maui-4
Mc-1	McKee-1
Mc-2	McKee-2
Mc-3	McKee-3A
Mc-4	McKee-4
Mo	Moki-1
Mot	Moturoa
P-1	Pouri-1
P	Pukearuhe-1
P-1B	Pukemai-1B
P-2	Pukemai-2
R-1	Republic-1
R-4	Republic-4
S	Stratford-1
S	Stratford-1
T-5	Taranaki-5
Ta-1	Tariki-1
T-1A	Tariki-1A
TT-1	ToeToe-1
TT-2B	ToeToe-2B
TT-3	ToeToe-3
TT-4	ToeToe-4
To	Toru-1
T-1	Tuhua-1
T-2	Tuhua-2
T-2	Tuhua-2, A-Sand
T-2	Tuhua-2, B-Sand
U	Urenui-1
W	Waihapa
WS	Waiotapu Seep
WaS	Waitangi Seep

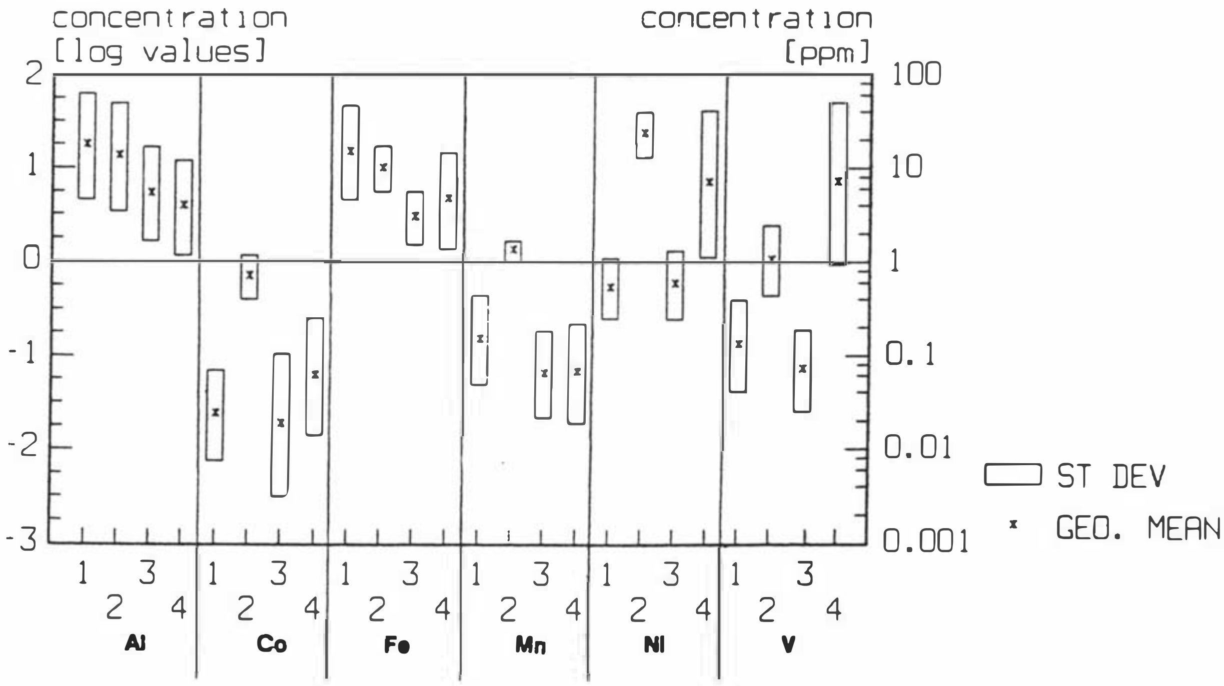
Figure 38: Arsenic (ng/g) versus Br (ng/g)



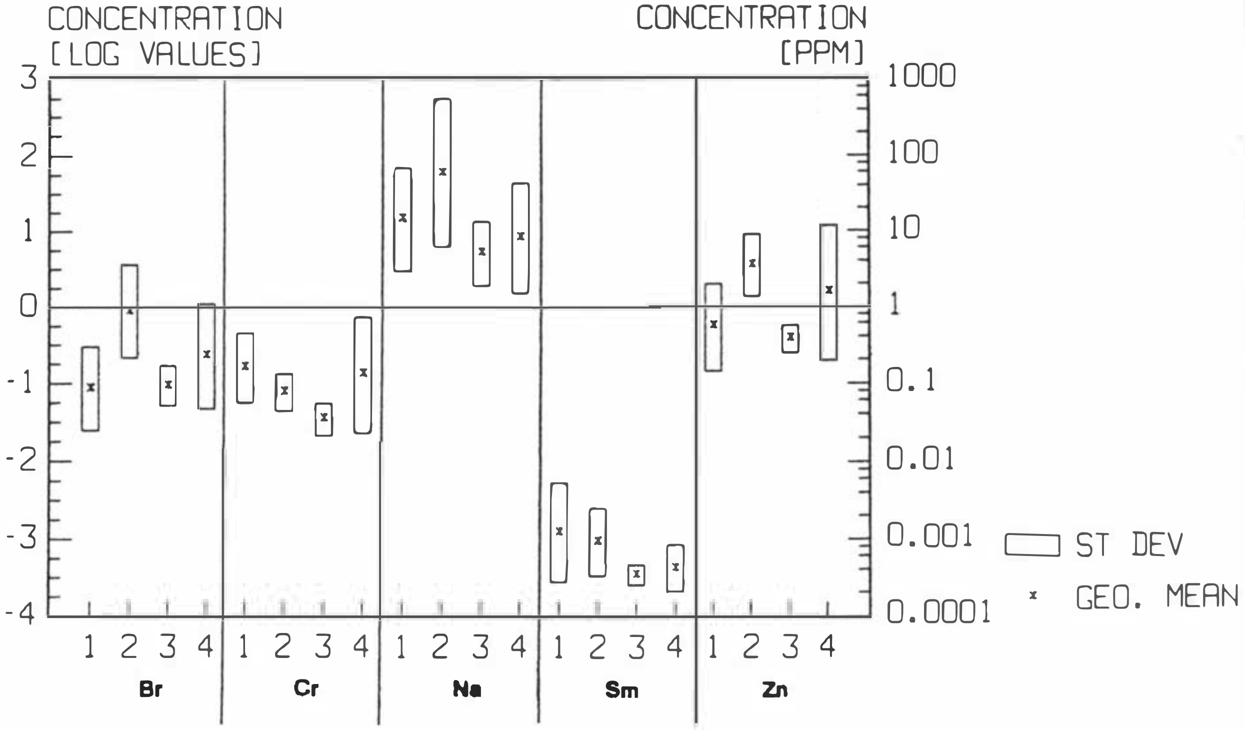
4.2. RELATIONSHIP OF NEW ZEALAND AND OVERSEAS CRUDE OILS

Trace element contents of all analysed overseas oils are listed in Appendices B and C. Samples include high to low maturity oils from various marine and terrestrial sources and different geographical areas. Most trace element concentrations are distinctly different in oils derived from terrestrial, lacustrine or marine source rocks. Most marine crude oils contain higher amounts of trace elements than oils from other sources, although high maturity marine oils are depleted in polar components and subsequently show low trace element concentrations.

Figure 39: Range (log concentrations and std. deviations) of trace element concentrations in New Zealand and overseas oils



1 = New Zealand oils
2 = lacustrine oils
3 = terrestrial oils
(Al, Ni and V include Australian oils from the Cooper/Eromanga Basin)
4 = marine oils



1 = New Zealand oils
2 = lacustrine oils
3 = terrestrial oils
4 = marine oils

4.2.1 Nickel and Vanadium

The Ni and V values in overseas oils range from less than 1 µg/g up to 150 µg/g Ni and 1200 µg/g V (*Tissot* and *Welte 1984*). *Barwise (1990)* was able to discriminate between oils from various origins, using Ni and V concentrations. These element concentrations can be used to separate oils from different sources, but as the element content also varies with maturity of oils, the resulting discrimination plots can only be used as an indication. *Barwise* showed that oils derived from source rocks with a high input of landplant matter (for example Gippsland Basin oils and oils derived from organic matter with input of more resinous material, such as Indonesian oils) usually contain less than 1 µg/g Ni and V. Crude oils originating from lacustrine source rocks usually show Ni/V ratios greater than 2, with ratios greater than 10 for some Chinese oils. Marine shales (e.g. Kimmeridge shale, North Sea), produce oils with moderate amounts of organic sulfur and a Ni/V ratio of 1 or less. High S oils contain high amounts of Ni and V and are usually derived from marine source rocks with little siliciclastic input. Vanadium is prevalent over Ni in these oils and they also contain moderate to high amounts of polar material. The maturity of oils affects their trace element content and high maturity oils, containing little polar material, show low concentrations of V and Ni.

Oils from the Taranaki Basin show Ni and V values that agree with the results for landplant-derived oils in the study of *Barwise (1990)*. Chinese oils of lacustrine origin from the Yumen Oilfields contain large amounts of Ni and their Ni/V ratios are greater than 18. The V content in Chinese oils, including oils from lacustrine source rocks, is very low with an average value of about 660 ng/g. Yumen oils contain about 4 times more V than New Zealand oils. Oils derived from sources comparable to Taranaki oils, especially the landplant-derived oil from Nigeria and the Taican-1 oil from China, show V and Ni concentrations very similar to New Zealand oils.

Crude oils from marine source rocks contain an average of 10 µg/g V and 3.9 µg/g Ni, with V values about 20 times and Ni values about 5 times higher than the New Zealand concentrations of these elements. The Ni and V contents in the Venezuelan crude oil are extremely high with values of 55.4 µg/g and 367 µg/g, respectively. The Venezuelan oil was not included in any graphs, as its trace element concentrations are far higher than in other marine and non-marine oils and the resulting plots did not show any discrimination between marine and terrestrial samples.

Marine oils with high maturity levels (North Sea and Middle East oil samples) that are depleted in polar components show Ni and V concentrations very similar to New Zealand oils. The North Sea and Middle East oil samples range from low to high maturity and show quite clearly that the metal content of oils decreases with increasing maturity.

A Ni versus V plot for terrestrial-derived oils (Figure 40) clearly distinguishes New Zealand oils from those of the Yumen Oilfields. The latter are derived from Cretaceous lacustrine source rocks and have migrated up to 40 km (*Luo, pers. comm.).* The Australian oils from the Cooper/Eromanga Basin contain Ni and V amounts very similar to those in New Zealand and other terrestrial-derived oils. The Ni and V concentrations in the Australian oils are relatively similar and most oils can be found in one large group (Figure 41). The V contents of these samples were mostly below the detection limit of INAA and values were calculated by taking the 60% value from the "less than" concentrations. The high Ni content could be characteristic of oils from lacustrine sources, as the Ni concentrations in lacustrine oils from the Uinta Basin are only slightly lower. Nickel values in the Nigerian landplant-derived oil, in Chinese oil derived from coal and in the Australian oil samples, are very similar to Ni concentrations in New Zealand oils. A Ni versus V graph for all New Zealand and overseas oils (Figure 42) shows quite clearly the low Ni and V content in New Zealand oils compared to marine sourced samples, as the New Zealand oils cluster in the bottom left corner of the plot. Los Angeles Basin oils and Yumen oils form two distinct groups, with oils from other areas spread around the graph. A plot of the log concentrations (Figure 42a) shows that high maturity marine oils with low element contents are not distinguishable from terrestrial oils. Oils from the same basin usually vary mainly in their V contents and contain very similar Ni concentrations. The differences might be partly due to errors involved in analysis, although Ni and V in overseas oils were determined by two different methods and the variations are usually larger than analytical or sampling errors.

LEGEND

1	*	Ahuroa-2
2	*	Blackwater
3	*	Galleon-1
4	*	Kaimiro-1
5	*	Kapuni Cond.
6	*	Kora-1 DST2
7	*	Kora-1 DST3
8	*	Kotuku Seep
9	*	Kupe South
10	*	Kupe-2
11	*	Kupe-3
12	*	Kupe-4
13	*	Kupe-5
14	*	Maui-1
15	*	Maui-3
16	*	Maui-4
17	*	McKee Cond.
18	*	McKee-2
19	*	McKee-3A
20	*	McKee-4
21	*	Moki-1
22	*	Moturoa
23	*	Pouri-1
24	*	Pukearuhe-1
25	*	Pukemai-1B
26	*	Pukemai-2
27	*	Republic-1
28	*	Republic-4
29	*	Stratford-1
30	*	Stratford-1
31	*	Taranaki-5
32	*	Tariki-1
33	*	Tariki-1A
34	*	ToeToe-1
35	*	ToeToe-2B
36	*	ToeToe-3
37	*	ToeToe-4
38	*	Toru-1
39	*	Tubua-1
40	*	Tubua-2
41	*	Tuhua-2, A-Sand
42	*	Tubua-2, B-Sand
43	*	Urenui-1
44	*	Waihapa
45	*	Waiotapu Seep
46	*	Waitangi Seep
47	Ch	Butouya China
48	Ch	Toucan-1, China
49	Ch	Taican-1, Ch
50	A	Timor Sea
51	Ni	Nigeria, landpl.
52	A	Merrimelia-6, Namur Sst.,
53	A	Merrimelia-6, Hutton
54	A	Merrimelia-6, Murta Member
55	A	Merrimelia-12
56	A	Strzelecki-3
57	A	Strzelecki-5
58	A	Strzelecki-10
59	A	Spencer-5, Birkhead
60	A	Spencer-5, Namur
61	A	Taloola-1
62	A	Tantanna-1
63	A	Dullingari-29, Murta Member
64	A	Dullingari-29, Namur Sst.
65	A	Lepena-1, Patchawarra
66	A	Lepena-1
67	A	Wancoocha-2, Murta Member
68	A	Wancoocha-2, Patchawarra
69	A	Wancoocha-2, Birkhead
70	A	Kidman-5
71	A	Meranji-1, Patchawarra
72	A	Meranji-1, Namur
73	A	Gidgealpa-16
74	A	Gidgealpa-17
75	A	Gidgealpa-20, Birkhead
76	A	Gidgealpa-20, Namur
77	A	Big Lake-37
78	A	Alwyn-1
79	A	Bagundi-1
80	A	Brumby-2
81	A	Florence-7A, San Juan Basin, USA
82	A	Florence-6A, San Juan Basin, USA
83	A	Mansfield-1A, San Juan Basin, USA
84	Y	Yumen #114, Jiuxi Basin, China,
85	Y	Yumen, #503
86	Y	Yumen, #502
87	Y	Yumen, #506
88	Y	Yumen, #507
89	Y	Yumen, #194
90	Y	Yumen, #68

*	New Zealand, oil samples
A	Australia, oil samples from the Cooper/Eromanga Basin
Ch	China, terrestrial oil samples
Ni	Nigeria, landplant-derived oil
US	U.S.A., oils from the San Juan Basin
Y	China, Jiuxi Basin, Yumen lacustrine-derived oil samples

Figure 40: Nickel (µg/g) and V (ng/g) in terrestrial-derived oils

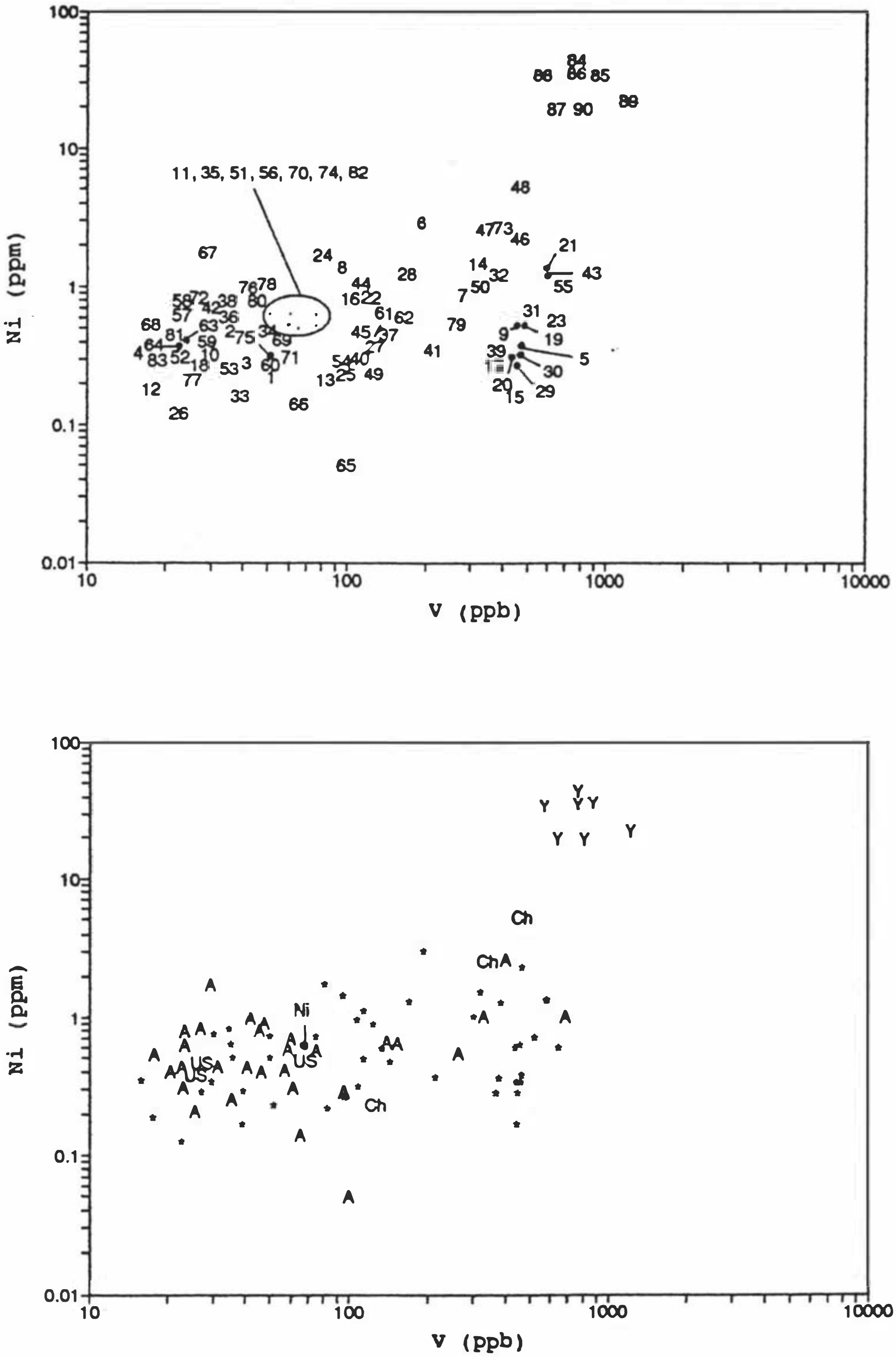
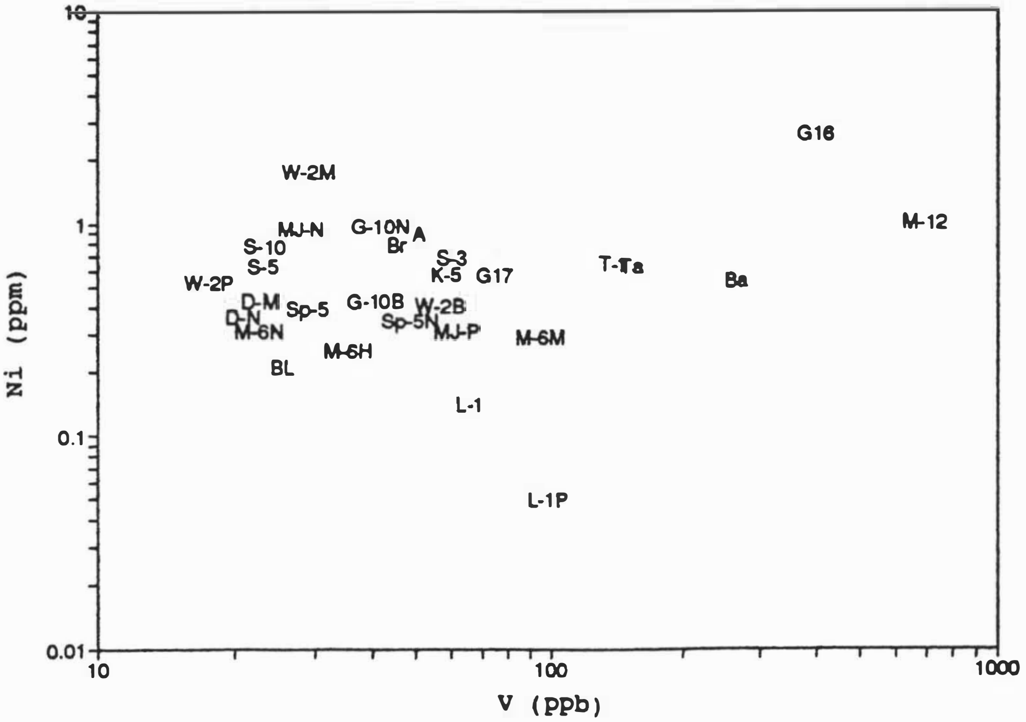


Figure 41: Nickel (µg/g) versus V (ng/g) for oils from the Cooper/Eromanga Basin, Australia

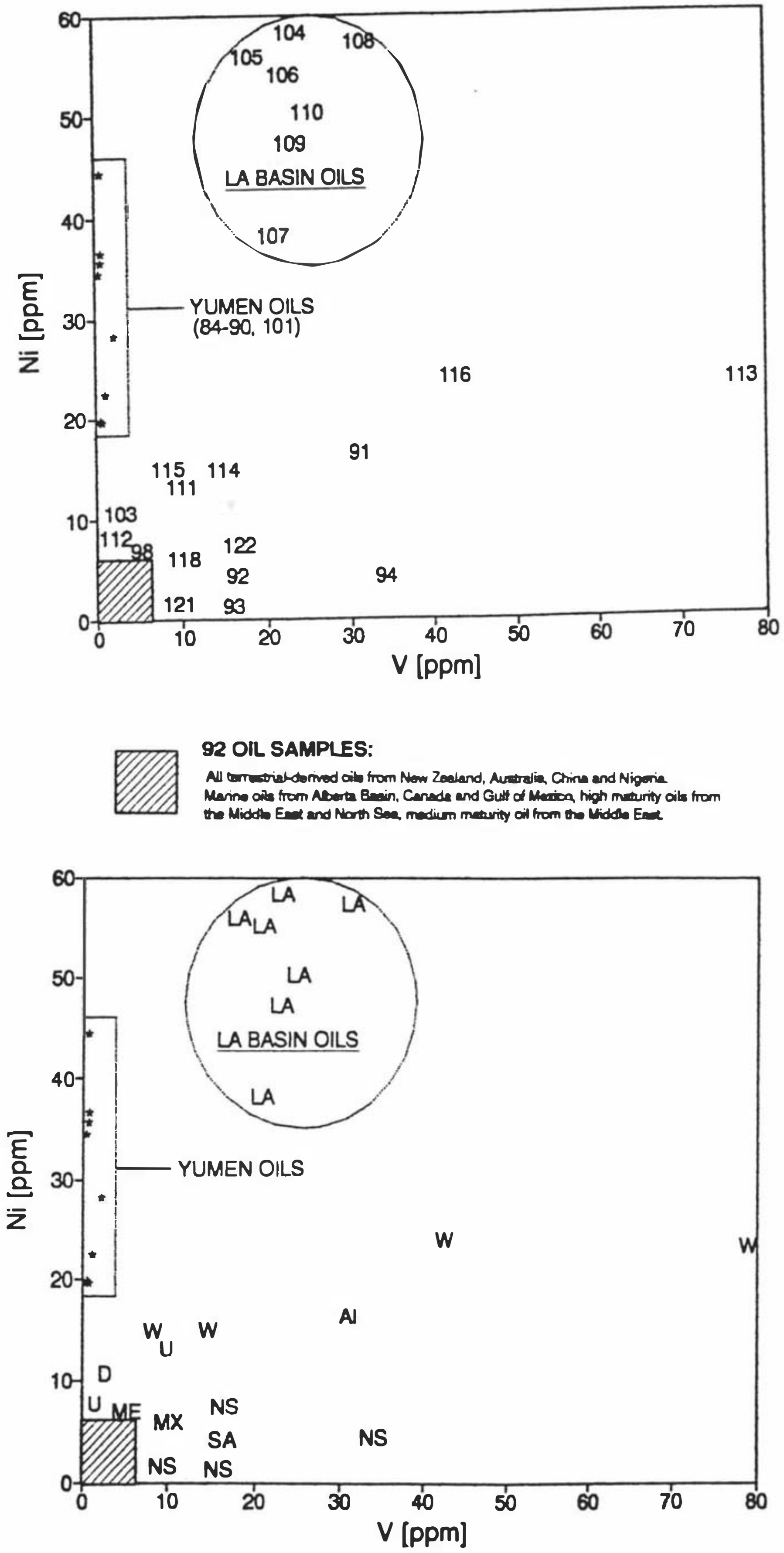


M-6N	Merrimelia-6, Namur Sst.
M-6H	Merrimelia-6, Hutton Sst.
M-6M	Merrimelia-6, Murta M.
M-12	Merrimelia-12
S-3	Strzelecki-3
S-5	Strzelecki-5
S-10	Strzelecki-10
Sp-5	Spencer-5, Birkhead Fm.
Sp-5N	Spencer-5, Namur Sst.
T-1	Taloola-1
Ta	Tantanna-1
D-M	Dullingari-29, Murta M.
D-N	Dullingari-29, Namur Sst.
L-1P	Lepena-1, Patchawarra Fm.
L-1	Lepena-1
W-2M	Wancoocha-2, Murta M.
W-2P	Wancoocha-2, Patchawarra Fm.
W-2B	Wancoocha-2, Birkhead Fm.
K-5	Kidman-5
MJ-P	Meranji-1, Patchawarra Fm.
MJ-N	Meranji-1, Namur Sst.
G16	Gidgealpa-16
G17	Gidgealpa-17
G-10B	Gidgealpa-20, Birkhead Fm.
G-10N	Gidgealpa-20, Namur Sst.
BL	Big Lake-37
A	Alwyn-1
Ba	Bagundi-1
Br	Brumby-2

LEGEND

1	*	Ahuroa-2
2	*	Blackwater
3	*	Galleon-1
4	*	Kaimiro-1
5	*	Kapuni Cond.
6	*	Kora-1 DST2
7	*	Kora-1 DST3
8	*	Kotuku Seep
9	*	Kupe South
10	*	Kupe-2
11	*	Kupe-3
12	*	Kupe-4
13	*	Kupe-5
14	*	Maui-1
15	*	Maui-3
16	*	Maui-4
17	*	McKee Cond.
18	*	McKee-2
19	*	McKee-3A
20	*	McKee-4
21	*	Moki-1
22	*	Moturoa
23	*	Pouri-1
24	*	Pukearuhe-1
25	*	Pukemai-1B
26	*	Pukemai-2
27	*	Republic-1
28	*	Republic-4
29	*	Stratford-1
30	*	Stratford-1
31	*	Taranaki-5
32	*	Tariki-1
33	*	Tariki-1A
34	*	ToeToe-1
35	*	ToeToe-2B
36	*	ToeToe-3
37	*	ToeToe-4
38	*	Toru-1
39	*	Tuhua-1
40	*	Tuhua-2
41	*	Tuhua-2, A-Sand
42	*	Tuhua-2, B-Sand
43	*	Urenui-1
44	*	Waihapa
45	*	Waiotapu Seep
46	*	Waitangi Seep
47	Ch	Butouya China
48	Ch	Toucan-1, China
49	Ch	Taican-1, Ch
50	A	Timor Sea
51	Ni	Nigeria, landpl.
52	A	Merrimelia-6, Namur Sst.,
53	A	Merrimelia-6, Hutton
54	A	Merrimelia-6, Murta Member
55	A	Merrimelia-12
56	A	Strzelecki-3
57	A	Strzelecki-5
58	A	Strzelecki-10
59	A	Spencer-5, Birkhead
60	A	Spencer-5, Namur
61	A	Taloola-1
62	A	Tantanna-1
63	A	Dullingari-29, Murta Member
64	A	Dullingari-29, Namur Sst.
65	A	Lepena-1, Patchawarra
66	A	Lepena-1
67	A	Wancoocha-2, Murta Member
68	A	Wancoocha-2, Patchawarra
69	A	Wancoocha-2, Birkhead
70	A	Kidman-5
71	A	Meranji-1, Patchawarra
72	A	Meranji-1, Namur
73	A	Gidgealpa-16
74	A	Gidgealpa-17
75	A	Gidgealpa-20, Birkhead
76	A	Gidgealpa-20, Namur
77	A	Big Lake-37
78	A	Alwyn-1
79	A	Bagundi-1
80	A	Brumby-2
81	A	Florence-7A, San Juan Basin, USA
82	A	Florence-6A, San Juan Basin, USA
83	A	Mansfield-1A, San Juan Basin, USA
84	Y	Yumen #114, Jiuxi Basin, China,
85	Y	Yumen, #503
86	Y	Yumen, #502
87	Y	Yumen, #506
88	Y	Yumen, #507
89	Y	Yumen, #194
90	Y	Yumen, #68
91	Al	Prudhoe Bay, Alaska
92	SA	Saudi-Arabia
93	NS	OMC 4755, North Sea, med. mat.
94	NS	OMC 3168, North Sea, low mat.
95	NS	OMC 5217, North Sea, high mat.
96	Ni	OMC 78, Nigeria, marine
97	ME	OMC 4677, Middle East, med. mat.
98	ME	OMC 5220, M. East, low mat.
99	ME	OMC 5363, M.East, high mat.
100	Ch	Quiketai Seep
101	Y	Yumen oilsand
102	Cb	Minghe Bridge oilsand
103	D	Dorset oilsand, U.K.
104	LA	154627 A (Hondo-3, Los Angeles)
105	LA	154627 B (Hondo-5)
106	LA	154627 D (Hondo-9)
107	LA	154627 E (Hondo-12)
108	LA	154627 F (Hondo-22)
109	LA	154627 H (Hondo-24)
110	LA	154627 K (Hondo-37)
111	U	19125 (Alfreda Knudsen-1, Uinta)
112	U	21850 (Orlan Johnson-1, Uinta)
113	W	22966 (Texas-1B, Williston)
114	W	22970 (R.P. Oliver-4, Will.)
115	W	22971 (Continental-1, Will.)
116	W	22974 (McAlister Fuel, Will.)
117	MX	41054 (Humble-3, G. of Mexico)
118	MX	41056 (Clark Oil Co. G. of Mex.)
119	Ca	48101 (Husky M. Rainbow, Alberta)
120	Ca	51577 (Imperial-Legal, Alb.)
121	NS	54051 A (25/11-1, North Sea)
122	NS	56323 (25/8-1, North Sea)

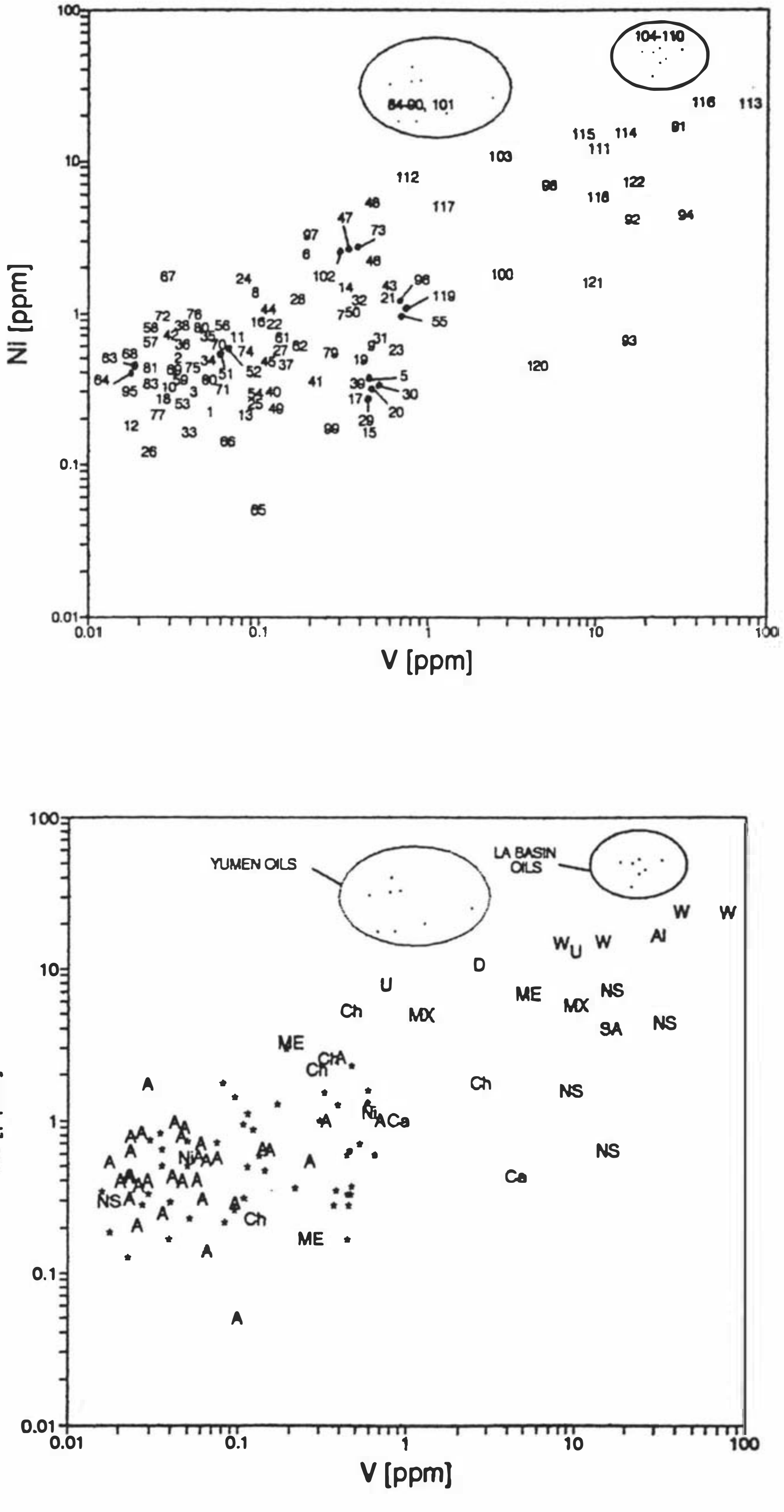
Figure 42: Nickel (µg/g) versus V (µg/g) for New Zealand and overseas oils



LEGEND

1	*	Ahuroa-2
2	*	Blackwater
3	*	Galleon-1
4	*	Kaimiro-1
5	*	Kapuni Cond.
6	*	Kora-1 DST2
7	*	Kora-1 DST3
8	*	Kotuku Seep
9	*	Kupe South
10	*	Kupe-2
11	*	Kupe-3
12	*	Kupe-4
13	*	Kupe-5
14	*	Maui-1
15	*	Maui-3
16	*	Maui-4
17	*	McKee Cond.
18	*	McKee-2
19	*	McKee-3A
20	*	McKee-4
21	*	Moki-1
22	*	Moturoa
23	*	Pouri-1
24	*	Pukearuhe-1
25	*	Pukemai-1B
26	*	Pukemai-2
27	*	Republic-1
28	*	Republic-4
29	*	Stratford-1
30	*	Stratford-1
31	*	Taranaki-5
32	*	Tariki-1
33	*	Tariki-1A
34	*	ToeToe-1
35	*	ToeToe-2B
36	*	ToeToe-3
37	*	ToeToe-4
38	*	Toru-1
39	*	Tuhua-1
40	*	Tuhua-2
41	*	Tuhua-2, A-Sand
42	*	Tuhua-2, B-Sand
43	*	Urenui-1
44	*	Waihapa
45	*	Waiotapu Seep
46	*	Waitangi Seep
47	Ch	Butouya China
48	Ch	Toucan-1, China
49	Ch	Taican-1, Ch
50	A	Timor Sea
51	Ni	Nigeria, landpl.
52	A	Merrimelia-6, Namur Sst.,
53	A	Merrimelia-6, Hutton
54	A	Merrimelia-6, Murta Member
55	A	Merrimelia-12
56	A	Strzelecki-3
57	A	Strzelecki-5
58	A	Strzelecki-10
59	A	Spencer-5, Birkhead
60	A	Spencer-5, Namur
61	A	Taloola-1
62	A	Tantanna-1
63	A	Dullingari-29, Murta Member
64	A	Dullingari-29, Namur Sst.
65	A	Lepena-1, Patchawarra
66	A	Lepena-1
67	A	Wancoocha-2, Murta Member
68	A	Wancoocha-2, Patchawarra
69	A	Wancoocha-2, Birkhead
70	A	Kidman-5
71	A	Meranji-1, Patchawarra
72	A	Meranji-1, Namur
73	A	Gidgealpa-16
74	A	Gidgealpa-17
75	A	Gidgealpa-20, Birkhead
76	A	Gidgealpa-20, Namur
77	A	Big Lake-37
78	A	Alwyn-1
79	A	Bagundi-1
80	A	Brumby-2
81	A	Florence-7A, San Juan Basin, USA
82	A	Florence-6A, San Juan Basin, USA
83	A	Mansfield-1A, San Juan Basin, USA
84	Y	Yumen #114, Jiuxi Basin, China,
85	Y	Yumen, #503
86	Y	Yumen, #502
87	Y	Yumen, #506
88	Y	Yumen, #507
89	Y	Yumen, #194
90	Y	Yumen, #68
91	Al	Prudhoe Bay, Alaska
92	SA	Saudi-Arabia
93	NS	OMC 4755, North Sea, med. mat.
94	NS	OMC 3168, North Sea, low mat.
95	NS	OMC 5217, North Sea, high mat.
96	Ni	OMC 78, Nigeria, marine
97	ME	OMC 4677, Middle East, med. mat.
98	ME	OMC 5220, M. East, low mat.
99	ME	OMC 5363, M.East, high mat.
100	Ch	Quiketai Seep
101	Y	Yumen oilsand
102	Ch	Minghe Bridge oilsand
103	D	Dorset oilsand, U.K.
104	LA	154627 A (Hondo-3, Los Angeles)
105	LA	154627 B (Hondo-5)
106	LA	154627 D (Hondo-9)
107	LA	154627 E (Hondo-12)
108	LA	154627 F (Hondo-22)
109	LA	154627 H (Hondo-24)
110	LA	154627 K (Hondo-37)
111	U	19125 (Alfreda Knudsen-1, Uinta)
112	U	21850 (Orlan Johnson-1, Uinta)
113	W	22966 (Texas-1B, Williston)
114	W	22970 (R.P. Oliver-4, Will.)
115	W	22971 (Continental-1, Will.)
116	W	22974 (McAlister Fuel, Will.)
117	MX	41054 (Humble-3, G. of Mexico)
118	MX	41056 (Clark Oil Co. G. of Mex.)
119	Ca	48101 (Husky M. Rainbow, Alberta)
120	Ca	51577 (Imperial-Legal, Alb.)
121	NS	54051 A (25/11-1, North Sea)
122	NS	56323 (25/8-1, North Sea)

Figure 42a: Nickel versus V (logarithmic concentrations) for New Zealand and overseas oils



The oils from the Cooper/Eromanga Basin in Australia contain Ni in concentrations comparable to New Zealand oils, with only a few values above the 1µg/g level. The V concentrations in the Australian oil samples were mostly below the limit of detection and concentrations used in graphs are 60% of the limit of detection value.

The Ni and V concentrations allow for discrimination of oils from different origins and further subdivision is probably possible for the marine and lacustrine oils of medium and low maturity. The low contents in terrestrial-derived oils and in marine oils of high maturity are prone to large errors and Ni and V concentrations cannot be used with confidence for classification of these oils into families.

4.2.2 Bromine and Chlorine

The Cl values in New Zealand oils are about 10 times lower than in marine oils and about 8 times lower than in other terrestrial oils. The Yumen oils show extremely high Cl concentrations with an average value of 2370 µg/g. This could be partly due to some water in the samples, as the Na values for Yumen oils lie well above the Na concentrations of other oils.

The Br content of the overseas samples follows the trend of the Cl concentrations. Yumen samples have the highest Br concentration with an average value of 2700 ng/g, with marine oils containing about 3 times less of this element. The Br content in terrestrial samples is very similar to the concentration of this element in New Zealand oils.

The Yumen oils were formed under anoxic conditions in a lake environment high in salt and have accumulated in reservoirs rich in salts and gypsum (*Collen, pers. comm.*). The high Br, Cl and Na concentrations reflect this quite clearly, although oils do not show increasing element content with increasing migration distance. Oils from the same field are also produced from different depths and layers of rock, which could account for the variations of the Br and Cl concentrations in oils from the same field.

4.2.3. Aluminium

The average Al concentration in New Zealand oils is about 4 times higher than in marine oils, with the concentrations in Chinese oils below the detection limit. The Al content in marine oils is generally lower than in New Zealand oils and only oils extracted from sandstones contain high amounts of this element, probably due to mineral matter extracted with the hydrocarbons. Australian oil samples from the Cooper/Eromanga Basin contain relatively low amounts of Al (mean concentration of 17.32 µg/g), about half the mean concentration found in New Zealand samples. The variation of the Al content in the Australian oils is small, and this seems to further indicate that the high Al content and the large variation in the Al concentration in New Zealand oils might be due to contamination by clay.

4.2.4 Chalcophile elements: Cu, Zn, As, Se, Sb, Pb, Cd

Cu, Cd and Pb values vary only slightly between marine and New Zealand oils. The Zn concentrations in some marine oils e.g. some Middle East and North Sea oils, are very high. Other terrestrial-derived oils show Zn concentrations in the same range as New Zealand oils. The Yumen oil samples and other marine oils contain similar amounts of this element with the average amount about 4 times higher than in New Zealand oils. The highest amount of Zn is found in the Chinese Quiketai Seep oil (67 µg/g).

The As concentrations in the Hutoya oil sample and the oil extracted from the Dorset oilsand are very high compared to other oils. Arsenic levels in the Nigerian landplant derived oil and New Zealand oils are very similar, with the As concentrations in the Yumen oils about 3 times higher than in marine oils.

Concentrations of Sb show little variations between the different oils and most Se levels were below the detection limit in overseas oils.

4.2.5. Siderophile elements: Fe, Co, Mo, Cr, Mn

The Fe content in New Zealand oils is slightly higher than in concentrations of this element in marine oils. The Chinese lacustrine oils contain about one third less Fe than marine oils and the average value in terrestrial-derived oils is about 8 times lower than in New Zealand oils. The highest Fe content was detected in the oil extracted from the Dorset oilsand (93.1 µg/g) and is probably due to co-extracted mineral matter.

Manganese follows the trend of Fe very closely with levels in terrestrial and lacustrine oils lower than in marine and New Zealand oils by about the same factor. The highest concentrations can be found in the New Zealand oils.

The concentrations of Co, an element usually bound to the polar organic oil fractions, are extremely low in New Zealand and other terrestrial derived oils. The Toucan-1 oil is an exception, as its Co value is about 10 times higher and similar to the Maui-1 and Maui-4 oils. The Yumen oils show exceptionally high Co concentrations, that are about 5 to 10 times higher than in marine oils. The same trend can be observed in the lacustrine derived oils from the Uinta Basin, which contain slightly higher Co concentrations than other marine oils. As the Ni contents in lacustrine oils are very high, the high Co concentrations are not surprising, as these two elements are closely related chemically.

The Cr concentrations in two Middle East oils (2642 µg/g and 1253 µg/g) and the Quiketai seep oil (6240 µg/g) are very high. All other oils, including most marine oils, show levels slightly below the Cr concentrations in New Zealand oils.

All siderophile elements are present in lower concentrations in terrestrial-derived oils from China and Nigeria and the relatively high concentrations of Cr, Fe and Mn in New Zealand oils are likely to be due to contamination by clay minerals. Only Co and Mn levels decrease with increasing maturity, indicating that they are closely associated with the organic, highly polar fractions in crude oils.

4.2.6. Rare earth elements: Eu, Sc, Sm

The rare earth elements are very evenly distributed in oils from different origins and no great variations can be observed. High levels of Eu, Sc and Sm are present in hydrocarbons extracted from sandstones, probably due to co-extracted mineral and clay material. The Quiketai seep oil (China) contains high amounts of Sc, about 10000 times higher than in other oils. The Sc and Sm concentrations in New Zealand oils are higher than in any other overseas oils, supporting the theory that clays are partially responsible for the trace elements found in New Zealand oils.

4.2.7 Interelemental correlations

The correlation analysis including all New Zealand and overseas samples resulted in a large number of highly correlated element pairs due to the quantity of samples involved. The correlation matrices of landplant derived oils, lacustrine and landplant derived oils and marine oils provide more information about the relationship of elements in overseas oils (Figures 43, 44 and 45).

Terrestrially derived oils show highly significant correlations only for Mn/Fe and Co/Ni, elements chemically closely related. None of the correlation coefficients in marine oils are very highly significant and only siderophile elements (Co/Fe, Co/Ni, Fe/Mn) correlate highly. Overseas oils do not show any correlations between clay elements, as observed in New Zealand oils, supporting the theory that New Zealand oils contain clay minerals. A graph of Al versus V (Figure 46), that resulted in an almost linear relationship between New Zealand oils, shows the different behaviour of all overseas oils.

Plots of Co versus Mn (Figure 47) of terrestrially derived oils clearly separate the Yumen oils from the rest, but show the similarities in concentrations of other landplant derived oils. Other graphs including the marine oil samples resemble the Ni versus V graph in Figure 42. A clear separation of marine and lacustrine oils from terrestrial-sourced oils is visible, but little additional information can be obtained from them. High maturity marine oils and other terrestrial oils are not distinguishable from New Zealand oils based on their trace element concentrations.

Figure 43: Correlation matrix for terrestrial-derived oils (excluding NZ oils)

	Al	As	Br	Cl	Co	Cr	Cs	Eu	Fe	Mn	Na	Ni	Sb	Sc	Sm	V	Zn
Al		S^{*}	S^{**}	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	S^{*}	NS	NS
As			S^{*}	S	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	S	NS	NS
Br				NS	NS	NS	NS	NS	NS	NS	NS	NS	S	NS	NS	NS	NS
Cl					S	NS	NS	NS	NS	NS	NS	S	NS	NS	S	NS	NS
Co						NS	NS	S	NS	NS	NS	S	NS	NS	NS	S	NS
Cr							NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	S
Cs								S	NS	NS	NS	NS	NS	S	NS	NS	NS
Eu									NS	NS	NS	NS	NS	NS	NS	NS	NS
Fe										S	NS	NS	NS	NS	NS	S^{*}	NS
Mn											NS	NS	NS	NS	NS	S	NS
Na												NS	NS	NS	NS	NS	NS
Ni													NS	NS	NS	S	S
Sb														NS	NS	NS	NS
Sc															NS	NS	NS
Sm																NS	NS
V																	NS

S^{**} very highly significant, $r > 0.951$ ($P < 0.001$)
S^{*} highly significant, $0.874 < r \le 0.951$ ($0.001 \le P < 0.01$)
S significant, $0.754 \le r < 0.874$ ($0.01 \le P < 0.05$)
NS not significant

Figure 44: Correlation matrix for lacustrine oils

	Al	As	Br	Cl	Co	Cr	Cs	Eu	Fe	Mn	Na	Ni	Sb	Sc	Sm	V	Zn
Al		S^{*}	NS	S	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
As			NS	S^{*}	S	NS	NS	NS	S	NS	NS	NS	S	S	NS	NS	NS
Br				NS	NS	NS	S^{**}	S^{*}	NS	NS	S^{*}	NS	NS	NS	S^{**}	S	NS
Cl					NS	S^{*}	NS	NS	S	NS	NS	NS	S	S	NS	NS	NS
Co						NS	NS	NS	NS	NS	NS	S^{**}	NS	NS	NS	NS	NS
Cr							NS	NS	S	NS	NS	NS	NS	S	NS	S	NS
Cs								S	NS	NS	S	NS	NS	NS	S^{*}	NS	NS
Eu									NS	NS	NS	NS	NS	NS	S^{*}	NS	NS
Fe										S	NS	NS	NS	S^{*}	NS	NS	NS
Mn											NS	NS	NS	S^{*}	NS	NS	NS
Na												NS	NS	NS	S^{**}	NS	NS
Ni													NS	NS	NS	NS	NS
Sb														NS	NS	NS	NS
Sc															NS	NS	NS
Sm																NS	NS
V																	NS

S^{**} very highly significant, $r \geq 0.898$
S^{*} highly significant, $0.798 \leq r < 0.898$
S significant, $0.666 \leq r < 0.798$
NS not significant

Figure 45: Correlation matrix for marine oils

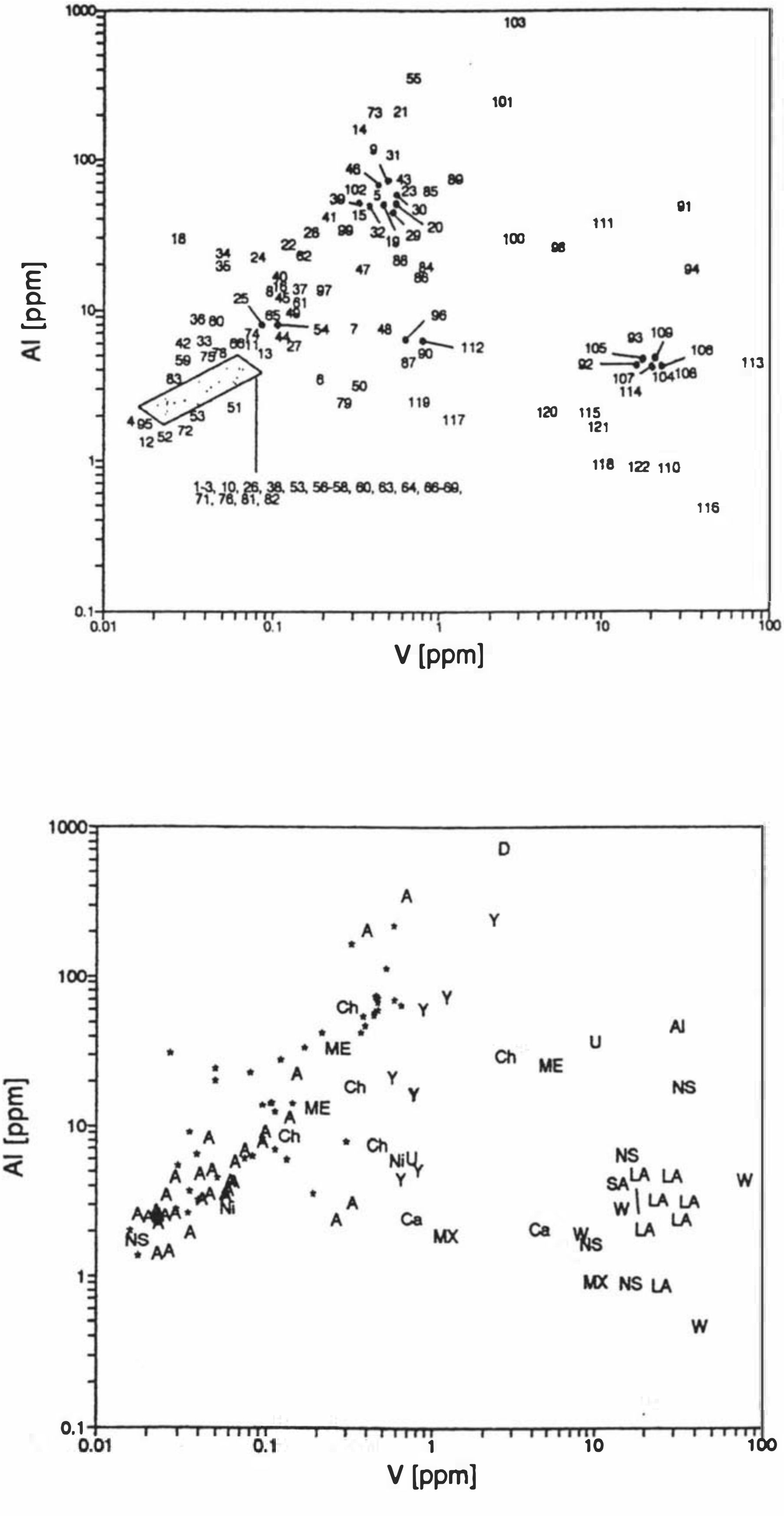
	Al	Co	Fe	Mn	Ni	V
Al		S	NS	S^{*}	NS	S
Co			S^{*}	NS	S^{*}	NS
Fe				S	S	NS
Mn					S	NS
Ni						NS

S^{**} very highly significant, $r > 0.597$ ($P < 0.001$)
S^{*} highly significant, $0.487 < r \leq 0.597$ ($0.001 \leq P < 0.01$)
S significant, $0.381 < r \leq 0.487$ ($0.01 \leq P < 0.05$)_
NS not significant

LEGEND

1	*	Ahuroa-2
2	*	Blackwater
3	*	Galleon-1
4	*	Kaimiro-1
5	*	Kapuni Cond.
6	*	Kora-1 DST2
7	*	Kora-1 DST3
8	*	Kotuku Seep
9	*	Kupe South
10	*	Kupe-2
11	*	Kupe-3
12	*	Kupe-4
13	*	Kupe-5
14	*	Maui-1
15	*	Maui-3
16	*	Maui-4
17	*	McKee Cond.
18	*	McKee-2
19	*	McKee-3A
20	*	McKee-4
21	*	Moki-1
22	*	Moturoa
23	*	Pouri-1
24	*	Pukearuhe-1
25	*	Pukemai-1B
26	*	Pukemai-2
27	*	Republic-1
28	*	Republic-4
29	*	Stratford-1
30	*	Stratford-1
31	*	Taranaki-5
32	*	Tariki-1
33	*	Tariki-1A
34	*	ToeToe-1
35	*	ToeToe-2B
36	*	ToeToe-3
37	*	ToeToe-4
38	*	Toru-1
39	*	Tuhua-1
40	*	Tuhua-2
41	*	Tuhua-2, A-Sand
42	*	Tuhua-2, B-Sand
43	*	Urenui-1
44	*	Waihapa
45	*	Waiotapu Seep
46	*	Waitangi Seep
47	Ch	Butouya China
48	Ch	Toucan-1, China
49	Ch	Taican-1, Ch
50	A	Timor Sea
51	Ni	Nigeria, landpl.
52	A	Merrimelia-6, Namur Sst.,
53	A	Merrimelia-6, Hutton
54	A	Merrimelia-6, Murta Member
55	A	Merrimelia-12
56	A	Strzelecki-3
57	A	Strzelecki-5
58	A	Strzelecki-10
59	A	Spencer-5, Birkhead
60	A	Spencer-5, Namur
61	A	Taloola-1
62	A	Tantanna-1
63	A	Dullingari-29, Murta Member
64	A	Dullingari-29, Namur Sst.
65	A	Lepena-1, Patchawarra
66	A	Lepena-1
67	A	Wancoocha-2, Murta Member
68	A	Wancoocha-2, Patchawarra
69	A	Wancoocha-2, Birkhead
70	A	Kidman-5
71	A	Meranji-1, Patchawarra
72	A	Meranji-1, Namur
73	A	Gidgealpa-16
74	A	Gidgealpa-17
75	A	Gidgealpa-20, Birkhead
76	A	Gidgealpa-20, Namur
77	A	Big Lake-37
78	A	Alwyn-1
79	A	Bagundi-1
80	A	Brumby-2
81	A	Florence-7A, San Juan Basin, USA
82	A	Florence-6A, San Juan Basin, USA
83	A	Mansfield-1A, San Juan Basin, USA
84	Y	Yumen #114, Jiuxi Basin, China,
85	Y	Yumen, #503
86	Y	Yumen, #502
87	Y	Yumen, #506
88	Y	Yumen, #507
89	Y	Yumen, #194
90	Y	Yumen, #68
91	Al	Prudhoe Bay, Alaska
92	SA	Saudi-Arabia
93	NS	OMC 4755, North Sea, med. mat.
94	NS	OMC 3168, North Sea, low mat.
95	NS	OMC 5217, North Sea, high mat.
96	Ni	OMC 78, Nigeria, marine
97	ME	OMC 4677, Middle East, med. mat.
98	ME	OMC 5220, M. East, low mat.
99	ME	OMC 5363, M.East, high mat.
100	Ch	Quiketai Seep
101	Y	Yumen oilsand
102	Ch	Minghe Bridge oilsand
103	D	Dorset oilsand, U.K.
104	LA	154627 A (Hondo-3, Los Angeles)
105	LA	154627 B (Hondo-5)
106	LA	154627 D (Hondo-9)
107	LA	154627 E (Hondo-12)
108	LA	154627 F (Hondo-22)
109	LA	154627 H (Hondo-24)
110	LA	154627 K (Hondo-37)
111	U	19125 (Alfreda Knudsen-1, Uinta)
112	U	21850 (Orlan Johnson-1, Uinta)
113	W	22966 (Texas-1H, Williston)
114	W	22970 (R.P. Oliver-4, Will.)
115	W	22971 (continental-1, Will.)
116	W	22974 (McAlister Fuel, Will.)
117	MX	41054 (Humble-3, G. of Mexico)
118	MX	41056 (Clark Oil Co. G. of Mex.)
119	Ca	48101 (Husky M. Rainbow, Alberta)
120	Ca	51577 (Imperial-Legal, Alb.)
121	NS	54051 A (25/11-1, North Sea)
122	NS	56323 (25/8-1, North Sea)

Figure 46: Aluminium (µg/g) versus V (µg/g) for New Zealand and overseas oils



LEGEND

1	*	Ahuroa-2
2	*	Blackwater
3	*	Galleon-1
4	*	Kaimiro-1
5	*	Kapuni Cond.
6	*	Kora-1 DST2
7	*	Kora-1 DST3
8	*	Kotuku Seep
9	*	Kupe South
10	*	Kupe-2
11	*	Kupe-3
12	*	Kupe-4
13	*	Kupe-5
14	*	Maui-1
15	*	Maui-3
16	*	Maui-4
17	*	McKee Cond.
18	*	McKee-2
19	*	McKee-3A
20	*	McKee-4
21	*	Moki-1
22	*	Moturoa
23	*	Pouri-1
24	*	Pukearuhe-1
25	*	Pukemai-1B
26	*	Pukemai-2
27	*	Republic-1
28	*	Republic-4
29	*	Stratford-1
30	*	Stratford-1
31	*	Taranaki-5
32	*	Tariki-1
33	*	Tariki-1A
34	*	ToeToe-1
35	*	ToeToe-2B
36	*	ToeToe-3
37	*	ToeToe-4
38	*	Toru-1
39	*	Tuhua-1
40	*	Tuhua-2
41	*	Tuhua-2, A-Sand
42	*	Tuhua-2, B-Sand
43	*	Urenui-1
44	*	Waihapa
45	*	Waiotapu Seep
46	*	Waitangi Seep
47	Ch	Butouya China
48	Ch	Toucan-1, China
49	Ch	Taican-1, Ch
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55	A	Merrimelia-12
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57	A	Strzelecki-5
58	A	Strzelecki-10
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61	A	Taloola-1
62	A	Tantanna-1
63	A	Dullingari-29, Murta Member
64	A	Dullingari-29, Namur Sst.
65	A	Lepena-1, Patchawarra
66	A	Lepena-1
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78	A	Alwyn-1
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81	A	Florence-7A, San Juan Basin, USA
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87	Y	Yumen, #506
88	Y	Yumen, #507
89	Y	Yumen, #194
90	Y	Yumen, #68
91	Al	Prudhoe Bay, Alaska
92	SA	Saudi-Arabia
93	NS	OMC 4755, North Sea, med. mat.
94	NS	OMC 3168, North Sea, low mat.
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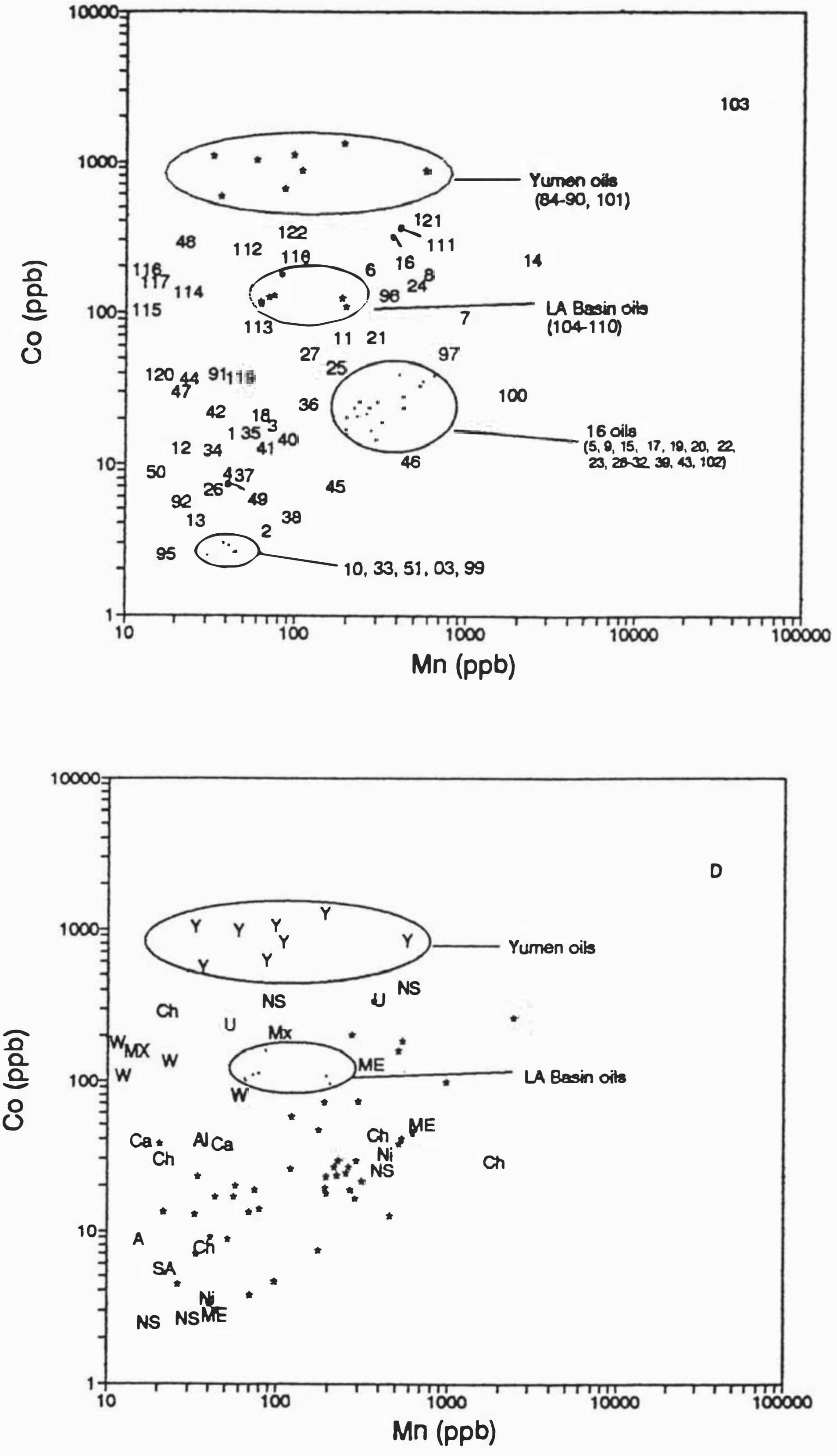
119	Ca	48101 (Husky M. Rainbow, Alberta)
120	Ca	51577 (Imperial-Legal, Alb.)
121	NS	54051 A (25/11-1, North Sea)
122	NS	56323 (25/8-1, North Sea)

Figure 47: Cobalt (ng/g) versus Mn (ng/g) for New Zealand and overseas oils (without samples 52-83, Australian oils)



4.3 SOURCE ROCK EXTRACTS AND THEIR RELATIONSHIP TO NEW ZEALAND OILS

A direct comparison of the trace element contents in rock extracts and crude oils is not possible, as element concentrations in extracts are higher due to the different chemical composition. Bitumen contains a higher percentage of polar components, able to complex trace elements, and possibly some mineral matter that has been extracted from the original rock sample.

Extracts of pyrolysed North Cape coal contained trace element concentrations comparable to the bitumen that was extracted from this sample before pyrolysis. All other pyrolysed extracts show increased contents of As, Br, Co, Ni, Sm, and Zn. The V concentrations were considerably lower than in other extracts, indicating that V is not incorporated in hydrocarbons produced by pyrolysis and a large part of the V content in other extracts is probably derived from extracted mineral or clay matter.

The Waipawa Black Shale extract (East Coast) contains about 8 times more Ni, but only slightly more V, than coal extracts from Taranaki and the South Island. Additionally, the Zn, Sm and Sc contents are higher, a fact that can also be observed in the Waitangi Seep oil. As biomarker and maturity studies suggest that the Waipawa shale is probably not the source of the Waitangi oil, the element levels might be coincidental, or some of the elements have been picked up by the oil during migration through layers of the Waipawa shale. The Toko-1 coal extracts showed very high concentrations of As, Br and Sm, with all other element concentrations in the same range as other bitumens. The Toko samples were treated with $CHBr_3$ to separate the coal fraction from other particles. A substantial amount of Br was obviously retained by the samples, although the coal fraction was washed and dried before extraction.

It is not possible to show a definite relationship of the South Island coals to the Taranaki oils, as trace element contents in the extracts and oils vary widely. The Maui-4 oil contained slightly more Co than other oils, but this fact alone is not sufficient to establish a definite correlation between the oil and the extract.

Extracts of the Yumen sample, likely to be the source of the Yumen oils, showed high levels of Ni and Co, in accordance with the high Ni and Co contents observed in the Yumen oils. Bromine and Cl in the Yumen rock extract were found in the same amounts as in other extracts, indicating that these elements in the Yumen oils were probably picked up during migration or in the reservoirs, as concentrations of these elements are extremely high in the oils.

A comparison of the total trace element content in coals and coal bitumen supplied no additional information. Elements found in high concentrations in coal are usually present in relatively high concentrations in the extracts, showing that certain percentages are complexed by the extractable organic matter. Bitumen from well cuttings and coal outcrops showed large variations in trace element concentrations, but no trend linking the coals to the Taranaki oils was apparent.

The extracts of the Kapuni-8 mudstone and coal samples contained high concentrations of Al, Br, Cl, Fe, Ni, Sb and Sc, with levels of V and other elements similar to other extracts. Vanadium seems to be present in low concentrations in various rocks in the Taranaki Basin, indicating that the depositing environment was low in this trace element or that conditions did not favour the complexing of V in organic compounds or even in clay minerals.

A statistical correlation analysis of New Zealand oils and bitumen was not very helpful, as the high number of samples resulted in many highly significant correlations. The significance of a given value of the correlation coefficient r depends on the number of degrees of freedom. A large number of samples results in highly significant correlations even with relatively low values of r. Statistical analysis of only the bitumen extracted from coal and well cuttings show strong correlations of As, Br and Sm (Figure 48). The high correlation observed for As and Br might be partly due to the extremely high concentrations of Br, caused by contamination of the Toko samples by $CHBr_3$. Arsenic is an element usually enriched in coal ash (*Mason* and *Moore 1982)* and is obviously extracted with the organic fraction of the coal.

Extracts of pyrolysed coals showed high correlations between Br/As, Eu/Al, Fe/Cs, and Ni/Mn. The relationship of elements in pyrolysed coals are very different to correlations obtained for oils. In graphs of As/Br, Co/Ni, Ni/V (Figures 49, 50 and 51), the pyrolysed coal extracts lie in a relatively tight cluster, indicating that the trace elements in the hydrocarbons produced by pyrolysis are very similar. The high Br concentrations in the Toko samples are due to contamination of the samples by $CHBr_3$. All other extracts show only little variations in their Br content.

Trace element concentrations of New Zealand oils and coal extracts were normalized by dividing their element contents by the appropriate Eu concentrations, as this element shows only little variations amongst oils of different areas and in extracts, to allow a direct comparison of oils and extracts.

Graphs of Ni versus V of New Zealand and overseas extracts (Figure 51 and 51a) show the differences between coals, Waipawa shale and Yumen extracts. The Waipawa black shale, Yumen and Kapuni mudstone extracts are distinctly different in their Ni and V concentrations to other New Zealand extracts. As the Ni and V concentrations in extracts are slightly higher than in oils, even after they were normalized with Eu, and all oils are separate from the extracts, no conclusion about their relationship can be drawn. A graph of As versus Br (Figure 49) shows the differences in the content of these two elements in Toko-1 coals. Graphs of other elements supply no further information about the relationship of oils and extracts as extracts usually lie separate, due to their higher element concentrations.

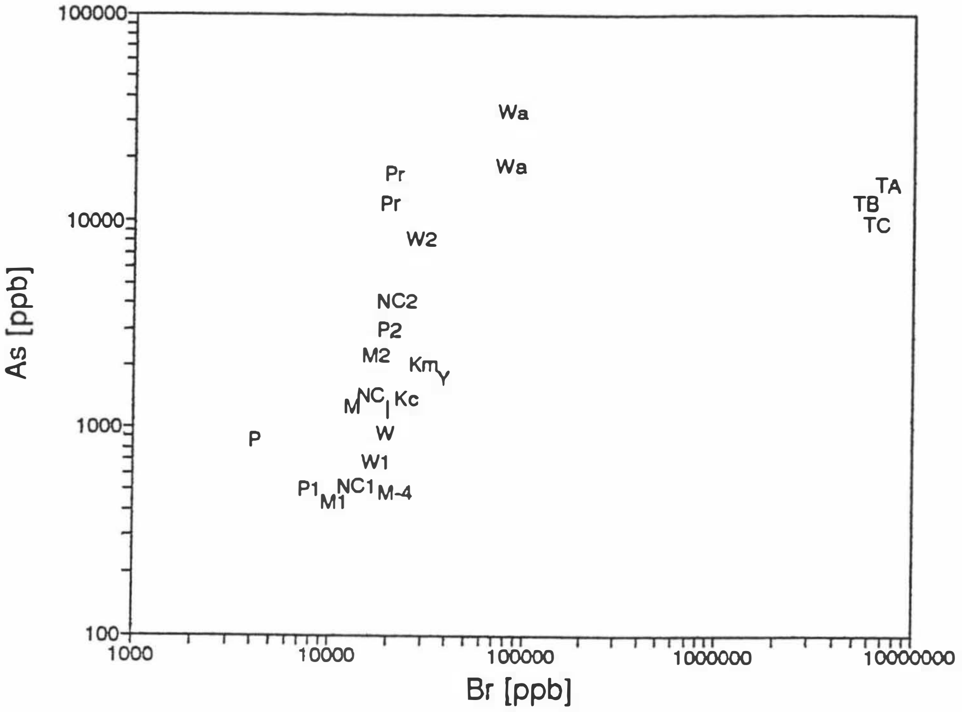
A definite connection of extracts of New Zealand coals and Taranaki oils is not possible, due to large differences in trace element contents and large variations in concentrations, despite

Figure 48: Correlation matrix for New Zealand bitumen

	Al	As	Br	Cl	Co	Cr	Cs	Eu	Fe	Mn	Na	Ni	Sb	Sc	Sm	V	Zn
Al		NS	NS	NS	NS	S	NS	NS	S	NS	NS	NS	NS	NS	NS	NS	NS
As			S^{**}	NS	S	NS	NS	NS	NS	NS	NS	NS	NS	NS	S^{**}	NS	NS
Br				NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	S^{**}	NS	NS
Cl					NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	S	NS	NS
Co						NS	NS	S	NS	NS	NS	S	NS	NS	NS	S	NS
Cr							S	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Cs								NS	NS	S	S	NS	NS	NS	NS	NS	NS
Eu									NS	NS	NS	NS	NS	NS	NS	NS	NS
Fe										NS	NS	NS	NS	NS	NS	NS	NS
Mn											NS	NS	NS	NS	NS	NS	NS
Na												NS	NS	NS	NS	NS	NS
Ni													NS	NS	NS	NS	NS
Sb														NS	NS	NS	NS
Sc															NS	NS	NS
Sm																NS	NS
V																	NS

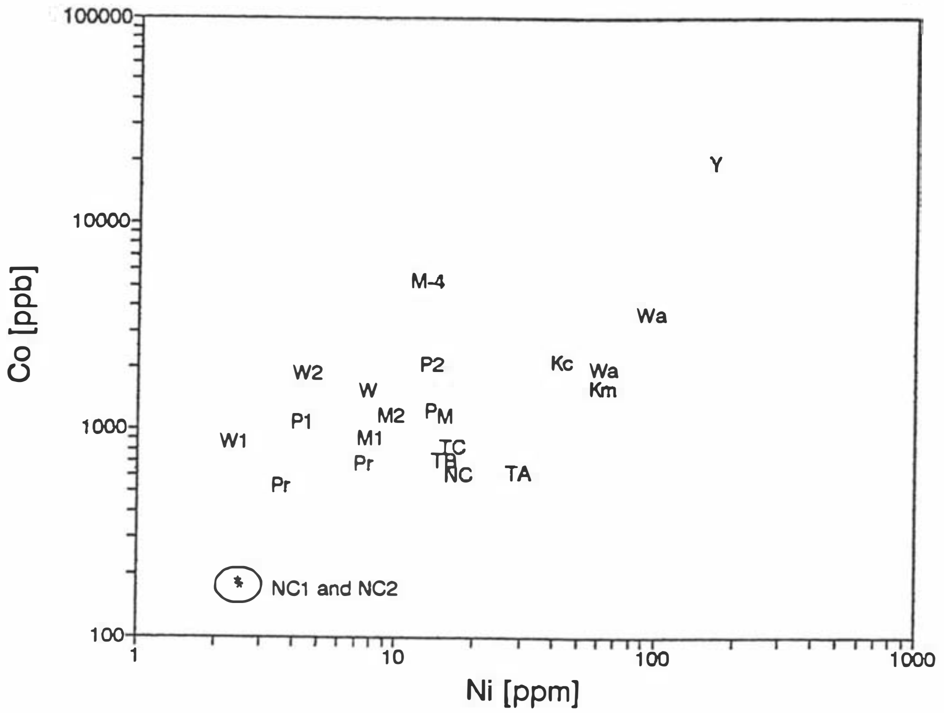
S^{**} very highly significant, $r > 0.872$ ($P < 0.001$)
S^{*} highly significant, $0.765 < r \leq 0.872$ ($0.001 \leq P < 0.01$)
S significant, $0.632 \leq r < 0.765$ ($0.01 \leq P < 0.05$)
NS not significant

Figure 49: Arsenic (ng/g) versus Br (ng/g) for bitumen



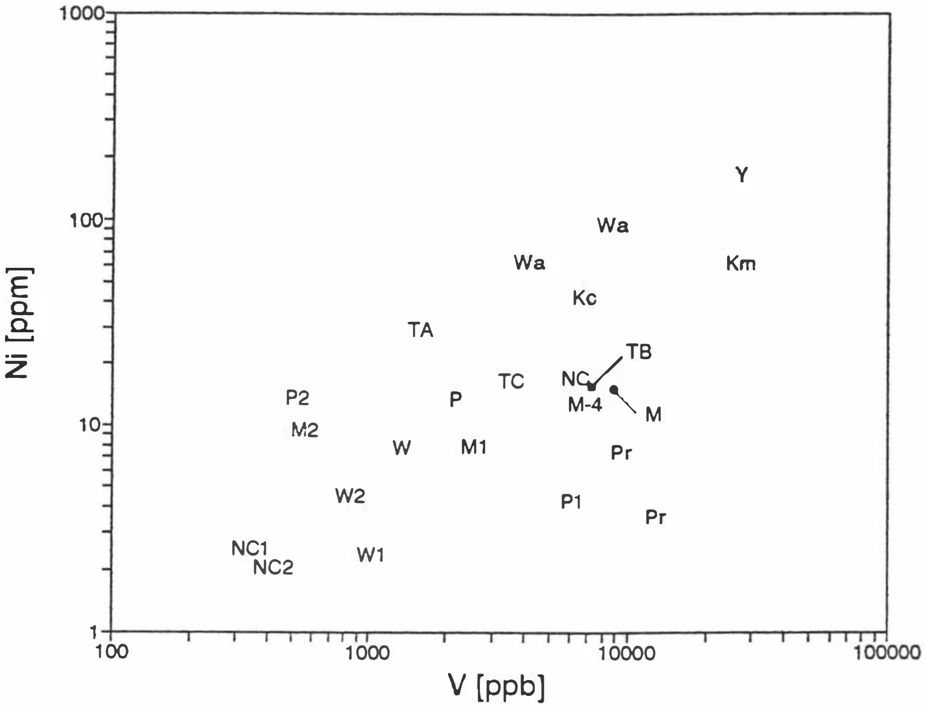
Y	Yumen rock
Wa	Waipawa Shale
Wa	Waipawa Shale O.Str.
Pr	Pritchard Bitumen
Pr	Pritchard B./carb.shale
M	Mangaraukau coal
W	Wairoa coal
P	Puponga coal
NC	North Cape coal
M-4	Maui-4 coal
TA	Toko-1,sample A
TB	Toko-1,sample B
TC	Toko-1,sample C
Kc	Kapuni #2 coal sample
Km	Kapuni #4 mudstone
W1	Wairoa Bit.I, before pyro.
M1	Mangarakau Bit.I, before pyro.
P1	Puponga Bit.I, before pyro.
NC1	North Cape Bit.I, before pyro.
NC2	North Cape Bit.II, after pyro.
W2	Wairoa Bit.II, after pyro
M2	Mangarakau Bit.II, after pyro.
P2	Puponga Bit.II, after pyro.

Figure 50: Cobalt (ng/g) versus Ni (µg/g) for bitumen



Y	Yumen rock
Wa	Waipawa Shale
Wa	Waipawa Shale O.Str.
Pr	Pritchard Bitumen
Pr	Pritchard B./carb.shale
M	Mangaraukau coal
W	Wairoa coal
P	Puponga coal
NC	North Cape coal
M-4	Maui-4 coal
TA	Toko-1,sample A
TB	Toko-1,sample B
TC	Toko-1,sample C
Kc	Kapuni #2 coal sample
Km	Kapuni #4 mudstone
W1	Wairoa Bit.I, before pyro.
M1	Mangarakau Bit.I, before pyro.
P1	Puponga Bit.I, before pyro.
NC1	North Cape Bit.I, before pyro.
NC2	North Cape Bit.II, after pyro.
W2	Wairoa Bit.II, after pyro
M2	Mangarakau Bit.II, after pyro.
P2	Puponga Bit.II, after pyro.

Figure 51: Nickel (µg/g) versus V (ng/g) for bitumen



Y	Yumen rock
Wa	Waipawa Shale
Wa	Waipawa Shale O.Str.
Pr	Pritchard Bitumen
Pr	Pritchard B./carb.shale
M	Mangaraukau coal
W	Wairoa coal
P	Puponga coal
NC	North Cape coal
M-4	Maui-4 coal
TA	Toko-1,sample A
TB	Toko-1,sample B
TC	Toko-1,sample C
Kc	Kapuni #2 coal sample
Km	Kapuni #4 mudstone
W1	Wairoa Bit.I, before pyro.
M1	Mangarakau Bit.I, before pyro.
P1	Puponga Bit.I, before pyro.
NC1	North Cape Bit.I, before pyro.
NC2	North Cape Bit.II, after pyro.
W2	Wairoa Bit.II, after pyro
M2	Mangarakau Bit.II, after pyro.
P2	Puponga Bit.II, after pyro.

standardising by their Eu concentration. Maui-4 oil and the Yumen oils cannot be linked with certainty to their respective extracts, despite some characteristic trace element contents. Statistical analysis of extracts resulted in very different trace element correlations than observed with elements in oils.

4.4 FORMATION WATERS

Most trace elements in the Formation well water samples of the Taranaki Basin are present in concentrations below the detection limit (Appendix J).

The samples show very high concentrations of cations associated with saline waters, such as Ca, K, Mg, Na. Potassium levels range from 80 µg/g to 34937 µg/g and Na values vary from 40 µg/g to 13992 µg/g. Elements found in the organic fractions of oils, such as Co and Ni, were not detected. Elements associated with clay minerals, such as Al, Cr, Mn, are present in amounts too small to be detected. Iron and Si are present in µg/g amounts, but variations are large.

Generally, the water samples show no concentration of elements associated with clay minerals. This does not exclude the possibility that clays have migrated with the water through the pore spaces, as minerals and ions behave very differently in water than in hydrocarbons. Ions and minerals present in water saturated rocks react readily with the surrounding minerals and grains, resulting in effectively closing the pore space. If hydrocarbons are introduced into this environment, the reactions stop as the water is only present in a fine film around the rock grains, prohibiting any ion exchange and reactions. Clay minerals that migrated with the water could have been lost by reactions with the surrounding rock and element concentrations could have changed through ion exchange reactions.

The trace element concentrations in New Zealand well water samples supply little information about their relationship to the oils or mineral matter picked up during migration.

4.5 PRINCIPAL COMPONENTS ANALYSIS

The data obtained were additionally subjected to different statistical treatments to separate related oils into different groups. Results of Factor and Cluster analyses, statistical procedures used in other studies, were not promising and these statistical techniques were regarded as unsuitable for the present project. Principal components analysis (PCA) showed the most potential in separating the New Zealand and overseas oils into different groups.

Principal components analysis is a statistical method used for finding one or more new variables (principal components) that convey as much as possible of the information contained in the original set of data. The number of related variables is reduced to a smaller set of uncorrelated variables. The variation in the first principal component accounts for as much as possible of the total variance in the data. The second principal component, at right angles to the first component, expresses the next highest possible variance and so forth. The main aim of PCA is to simplify the data. The first three principal components in the analysis of the New Zealand oils, New Zealand oils and bitumen and the two analyses of New Zealand and overseas oils accounted for over 70% (67.6%, 70.5%, 89.9% and 70.4% respectively) of the total variance of the original data.

4.5.1 New Zealand oils

The plots of principal component 1 (pc1) against pc2, pc1/pc3 and pc2/pc3 (Figure 52, 53 and 54) depict the differences in trace element concentrations in the samples.

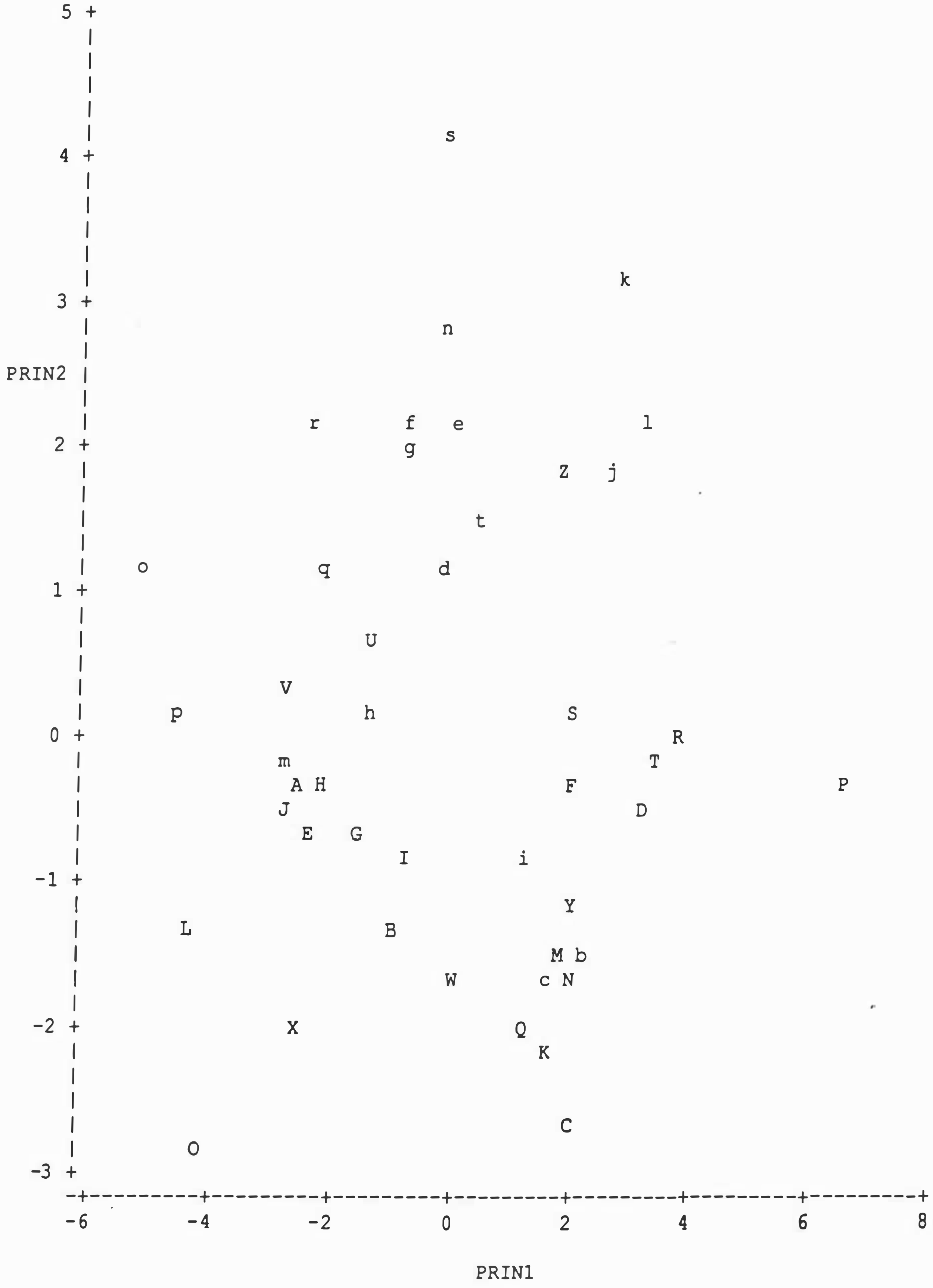
The pc graphs of New Zealand oils allow for a limited discrimination of oils. The Kotuku seep oil, Kora-1 and Maui-1 oils lie slightly apart from the rest of the crude oils in all three plots. Figure 54 (pc2/pc3) separates the two Kora-1 samples, Pukearuhe-1, Waiotapu and Kotuku Seep oils from other oils. The Kora-1 oils show a strong marine influence, recognizable by their biomarker content and absence of waxy aliphatic compounds. The two oils from DST2 and DST3 have the same source and are very similar, but they are produced from different horizons. One sample is from a sandstone reservoir, the other sample was produced from volcanic rock (*Reed 1991*), which could account for

LEGEND

A	Tuhua-2, B-Sand
B	Tuhua-2, A-Sand
C	Tuhua-1
D	Urenui-1
E	ToeToe-1
F	Tariki-1
G	ToeToe-4
H	ToeToe-2B
I	ToeToe-3
J	Kaimiro-1
K	Stratford-1
L	Pukemai-2
M	Pouri-1
N	McKee-4
O	Tariki-1A
P	Maui-1
Q	Maui-3
R	Moki-1
S	Republic-4
T	Taranaki-5
U	McKee-2
V	Blackwater
W	Galleon-1
X	Ahuroa-2
Y	McKee-3A
Z	Maui-4
a	Kupe South
b	Kapuni-1
c	McKee-1
d	Waiotapu Seep
e	Kotuku Seep
f	Pukemai-1B
g	Republic-1
h	Tuhua-2
i	Stratford-1
j	Pukearuhe-1
k	Moturoa
l	Waitangi Seep
m	Kupe-2
n	Kupe-3
o	Kupe-4
p	Kupe-5
q	Toru-1
r	Waihapa
s	Kora-1, DST2
t	Kora-1, DST3

Figure 52: Pc2/pc1 for New Zealand oils

```
Plot of PRIN2*PRIN1.  Symbol is value of ID.
```



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NOTE: 1 obs hidden.
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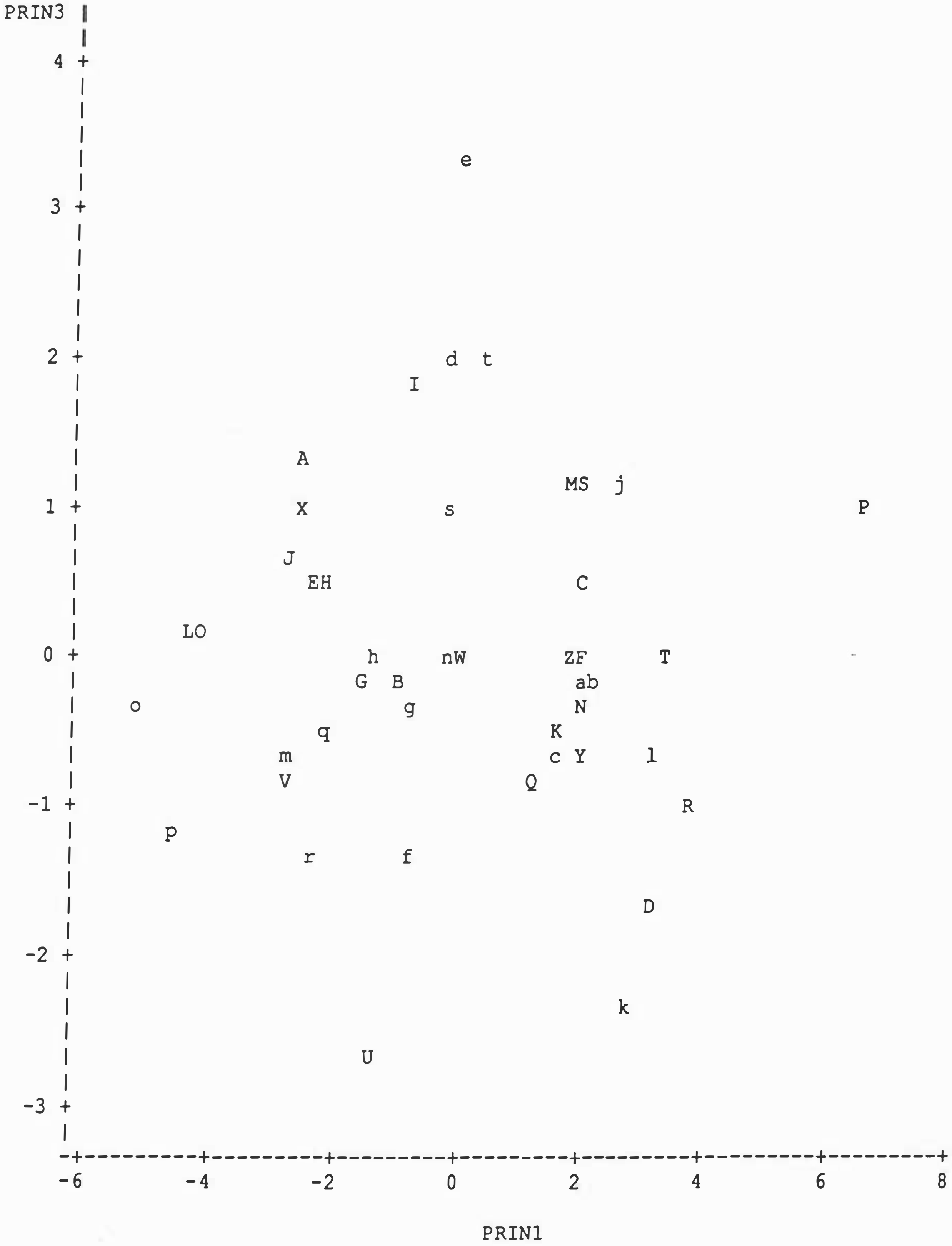
LEGEND

A	Tuhua-2, B-Sand
B	Tuhua-2, A-Sand
C	Tuhua-1
D	Urenui-1
E	ToeToe-1
F	Tariki-1
G	ToeToe-4
H	ToeToe-2B
I	ToeToe-3
J	Kaimiro-1
K	Stratford-1
L	Pukemai-2
M	Pouri-1
N	McKee-4
O	Tariki-1A
P	Maui-1
Q	Maui-3
R	Moki-1
S	Republic-4
T	Taranaki-5
U	McKee-2
V	Blackwater
W	Galleon-1
X	Ahuroa-2
Y	McKee-3A
Z	Maui-4
a	Kupe South
b	Kapuni-1
c	McKee-1
d	Waiotapu Seep
e	Kotuku Seep
f	Pukemai-1B
g	Republic-1
h	Tuhua-2
i	Stratford-1
j	Pukearuhe-1
k	Moturoa
l	Waitangi Seep
m	Kupe-2
n	Kupe-3
o	Kupe-4
p	Kupe-5
q	Toru-1
r	Waihapa
s	Kora-1, DST2
t	Kora-1, DST3

Figure 53: Pc3/pc1 for New Zealand oils

Plot of PRIN3*PRIN1. Symbol is value of ID.

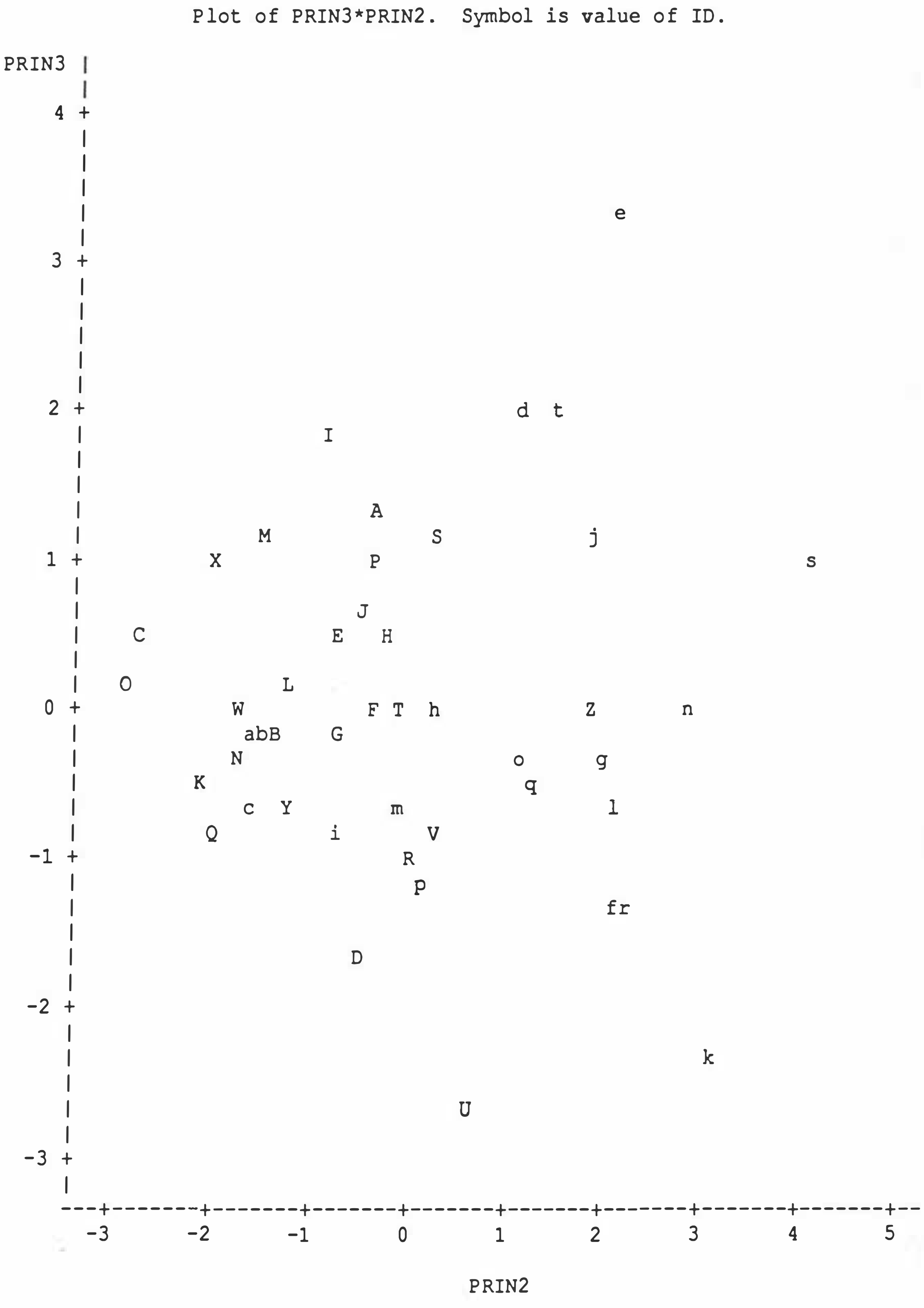


NOTE: 1 obs hidden.

LEGEND

A	Tuhua-2, B-Sand
B	Tuhua-2, A-Sand
C	Tuhua-1
D	Urenui-1
E	ToeToe-1
F	Tariki-1
G	ToeToe-4
H	ToeToe-2B
I	ToeToe-3
J	Kaimiro-1
K	Stratford-1
L	Pukemai-2
M	Pouri-1
N	McKee-4
O	Tariki-1A
P	Maui-1
Q	Maui-3
R	Moki-1
S	Republic-4
T	Taranaki-5
U	McKee-2
V	Blackwater
W	Galleon-1
X	Ahuroa-2
Y	McKee-3A
Z	Maui-4
a	Kupe South
b	Kapuni-1
c	McKee-1
d	Waiotapu Seep
e	Kotuku Seep
f	Pukemai-1B
g	Republic-1
h	Tuhua-2
i	Stratford-1
j	Pukearuhe-1
k	Moturoa
l	Waitangi Seep
m	Kupe-2
n	Kupe-3
o	Kupe-4
p	Kupe-5
q	Toru-1
r	Waihapa
s	Kora-1, DST2
t	Kora-1, DST3

Figure 54: Pc3/pc2 for New Zealand oils

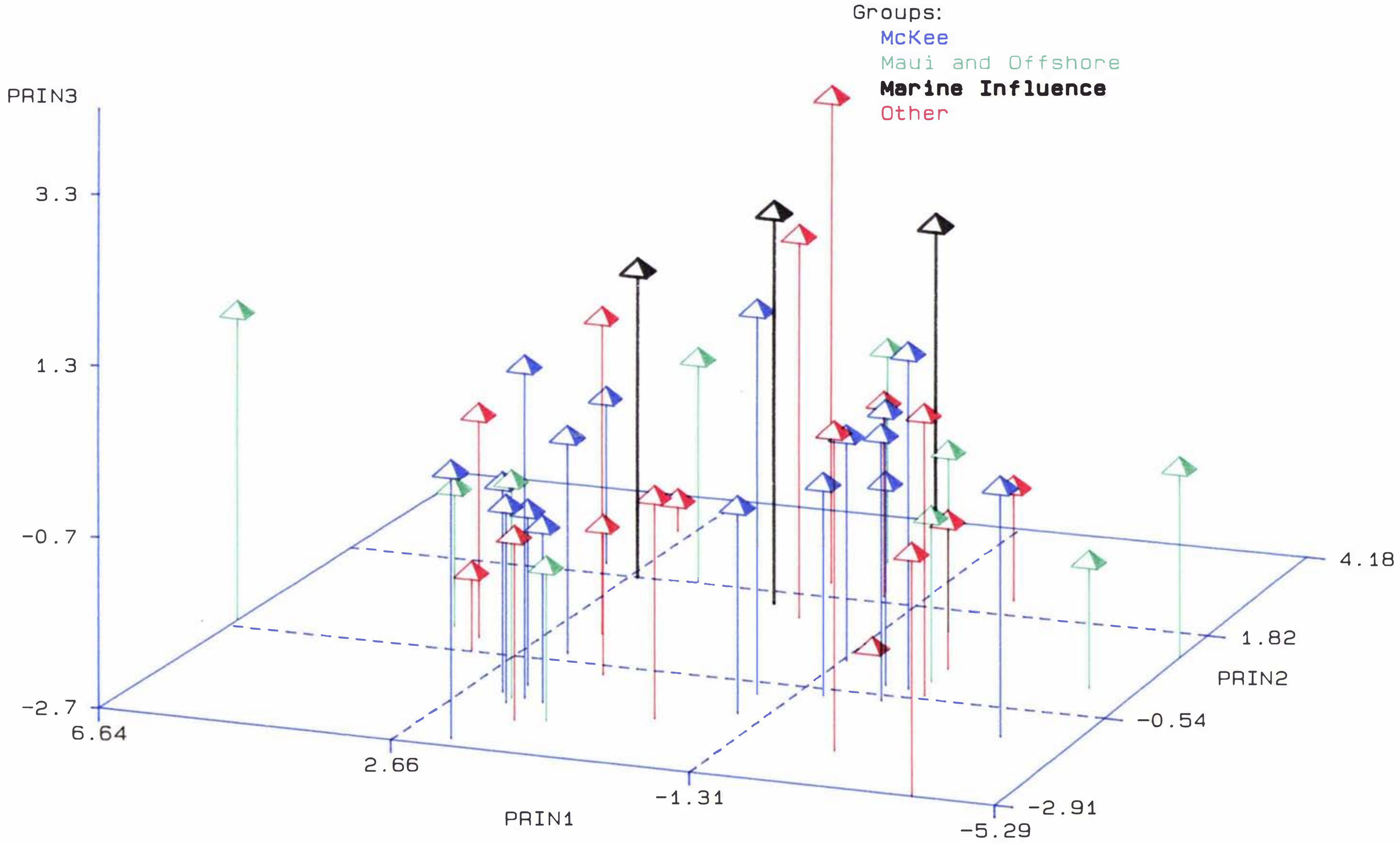


the differences in trace element composition. The McKee oils in the same graph occur in a relatively small band, with the exception of the Pukemai-1B oil. This sample consistently lies next to the Waihapa oil in all graphs. The oils from the shallow reservoirs (Moturoa, Taranaki-5 and Republic oils) are spread throughout the graph. The Waitangi and Kotuku seep oil samples are set apart from the rest of the oils. The Waiotapu seep oil though, was not singled out in any of the graphs.

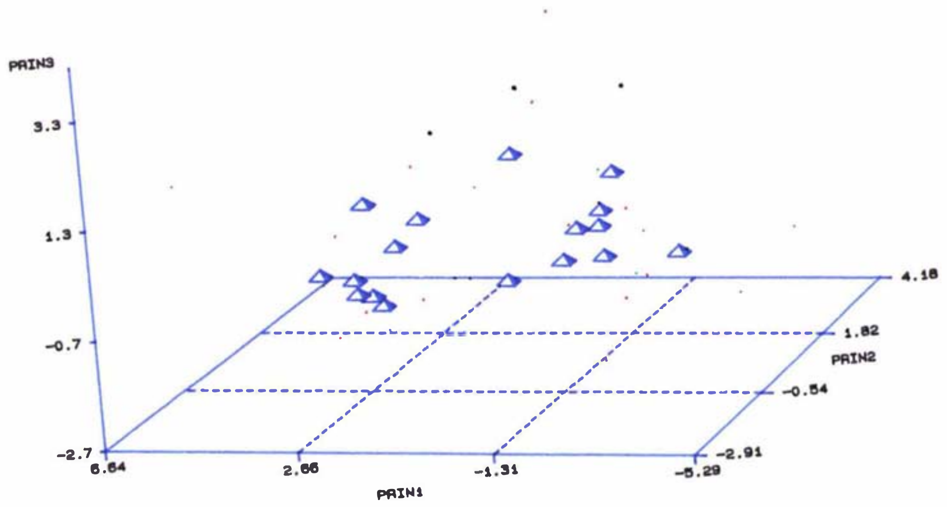
Three dimensional plots of New Zealand oil samples (Figure 55 and 55a) show that the McKee oils (group 1, blue) are spread widely throughout the graph and two clusters are distinguishable, with McKee-1, McKee-3, McKee-4, Tuhua-1 and Pouri-1 oils in the left bottom group, Pukemai-1B and Tuhua-2 in between the two groups and other McKee oils in the second cluster. Maui-1 lies separate, as do Kupe-4 and Kupe-5 oils (group 2, green). Group 3 (black) includes oils with marine influence (Kora samples, Pukearuhe) and this group plots slightly separate with the Kotuku and Waiotapu Seep oils (group 4, red). No definite groups of related oils are discernible. Oils from Taranaki basin are either very closely related and derived from the same or very similar source or their differences have been obscured by addition of trace elements by contamination or loss of elements by migration. The contamination by clays in some samples and not in others would effectively obscure any trend and differences, as PCA is based on the variances of trace element concentrations in oils. Clays could also be responsible for the relatively large variations in trace element concentrations and would obscure the fact that all Taranaki Basin oils are derived from the same source.

Figures 55 and 55a: Three dimensional graphs of principal components for New Zealand oils

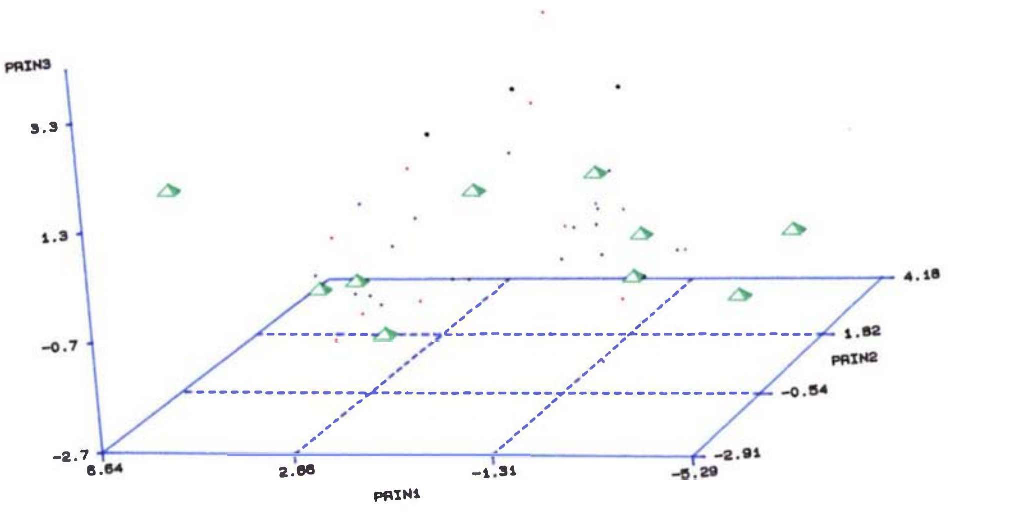
NZ OILS – ALL GROUPS



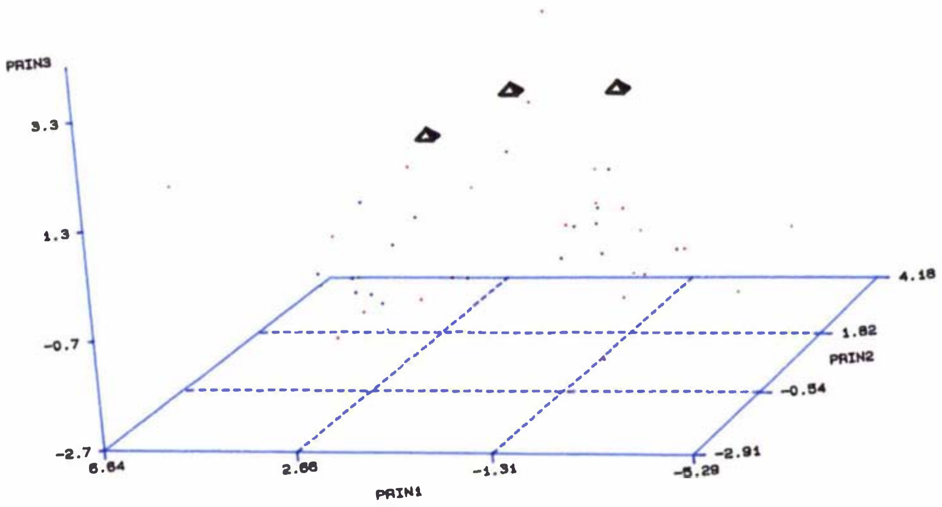
NZ OILS – MCKEE



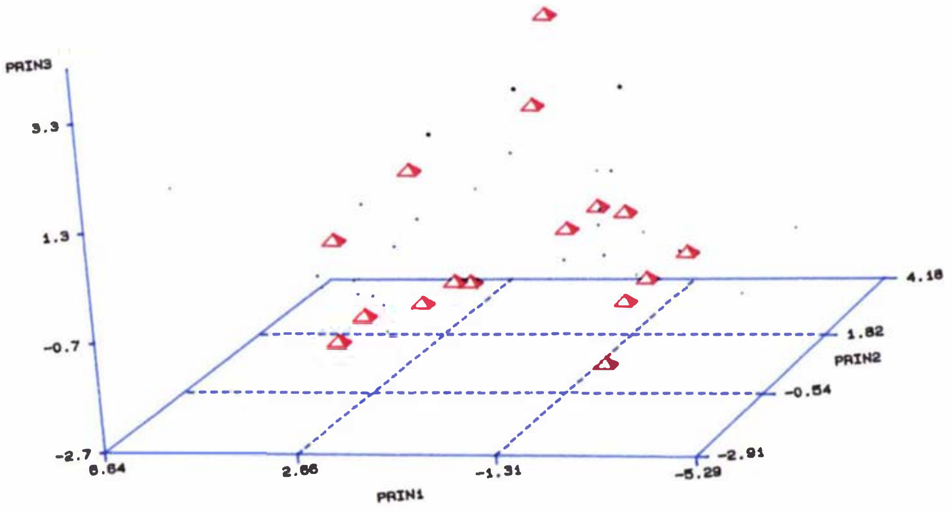
NZ OILS – MAUI AND



NZ OILS – MARINE INFLUENCE



NZ OILS – OTHER



4.5.2 New Zealand and Overseas oil

The principal components plots of New Zealand and overseas oils (Figures 56, 57, 58, 59, 60 and 61) show clear separation of lacustrine Yumen oils, Chinese seep oil, and oils extracted from oilsands. Figures 56, 57 and 58 are based on the statistical treatment of New Zealand and overseas oils based on 17 elements, whereas the principal components analysis for Figures 59, 60 and 61 included was based on 6 elements and included more marine oil samples. Australian oil samples were not included in the statistics, as only a few elements were determined in the samples. Only plots of pc1 against pc2 and pc2 against pc3 allow for clear discrimination of oils (Figures 56, 58, 59 and 61). All terrestrial-derived overseas oils, the marine-derived Nigerian oil and some of the North Sea and Middle east oils are distributed amongst the New Zealand samples. Oils of terrestrial origin and North Sea oils of high and medium maturity lie within the range of New Zealand oils. High maturity Middle East oils and all other marine and lacustrine oils are distinctly separate on the graphs. Marine and lacustrine oils from one basin are usually located in a relatively tight cluster in the graphs.

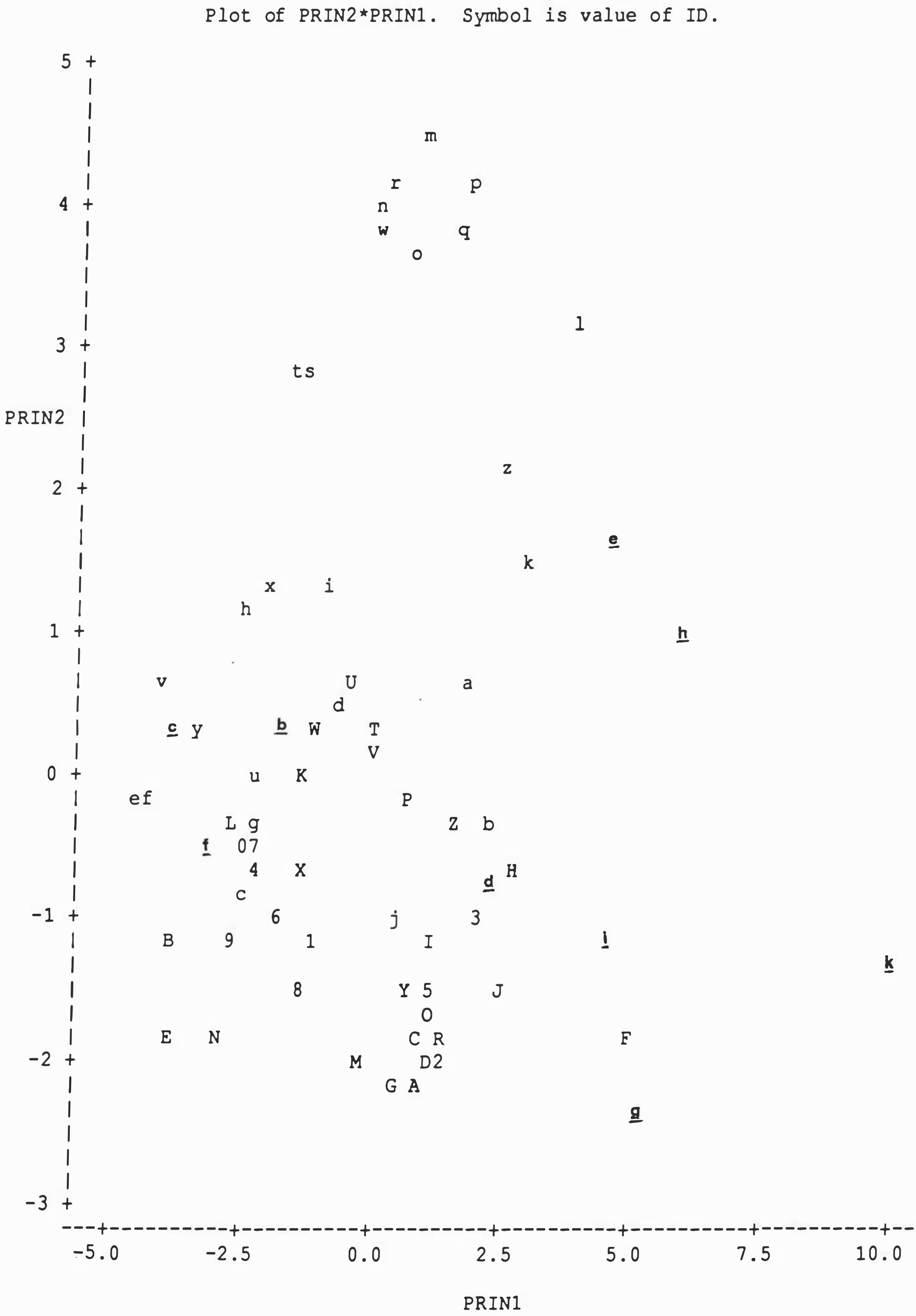
Three dimensional plots (Figures 62, 62a, 63 and 63a) show the New Zealand oils very widely spread around the plots, divided into two main groups with most marine and lacustrine oils spread on the outside edges. Many of the terrestrial-derived oils from China, Nigeria and Australia are located within the New Zealand oil clusters, as are marine oils with high and medium maturity. Oils derived from higher landplant matter exhibit very similar behaviour to New Zealand oils. The maturity of oils can have a large influence on their trace element concentrations and variations and the maturity differences of oils has to be taken into account, before any differentiation of oils into separate groups is attempted. One notable feature is the relatively tight cluster of lacustrine oils from the Jiuxi Basin, China. Related oils from the same basin seem to exhibit very similar variations in their trace element content, as could be observed by the small clusters of oils from the Jiuxi and Los Angeles basins (Figures 59, 60 and 61). The large variations of trace element concentrations in oils from the Taranaki Basin seem to indicate additional influences on their trace element content. Slight differences in maturity, as the oils are of similar but not identical maturities, could be responsible for some trace element variations, especially at

LEGEND

0	Tuhua-2, B-Sand	McKee Field
1	Tuhua-2, A-Sand	McKee Field
2	Tuhua-1	McKee Field
3	Urenui-1	
4	ToeToe-1	McKee Field
5	Tariki-1	
6	ToeToe-4	McKee Field
7	ToeToe-2B	McKee Field
8	ToeToe-3	McKee Field
9	Kaimiro-1	Condensate
A	Stratford-1	
B	Pukemai-2	Condensate
C	Pouri-1	McKee Field
D	McKee-4	McKee Field
E	Tariki-1A	Condensate
F	Maui-1	
G	Maui-3	Condensate
H	Moki-1	
I	Republic-4	
J	Taranaki-5	
K	McKee-2	McKee Field
L	Blackwater	Condensate
M	Galleon-1	Condensate
N	Ahuroa-2	Condensate
O	McKee-3A	McKee Field
P	Maui-4	
Q	Kupe South-1	
R	Kapuni-1	Condensate
S	McKee-1	McKee Field
T	Waiotapu	Seep
U	Kotuku	Seep
V	Pukemai-1B	McKee Field
W	Republic-1	
X	Tuhua-2	McKee Field
Y	Stratford-1	
Z	Pukearuhe-1	
a	Moturoa	
b	Waitangi	Seep
c	Kupe-2	
d	Kupe-3	
e	Kupe-4	
f	Kupe-5	
g	Toru-1	
h	Waihapa	
i	Kora-1, DST2	
j	Kora-1, DST3	
k	Venezuela	
l	Yumen #114	lacustrine oil, Juixi B.
m	Yumen, #503	lacustrine oil, Juixi B.
n	Yumen, #502	lacustrine oil, Juixi B.
o	Yumen, #506	lacustrine oil, Juixi B.
p	Yumen, #507	lacustrine oil, Juixi B.
q	Yumen, #194	lacustrine oil, Juixi B.
r	Yumen, #68	lacustrine oil, Juixi B.
s	Hutouya, China	terr. oil
t	Toucan-1, China	terr. oil, Turpan Basin

u	Taican-1, China	terr. oil, Turpan Basi
v	Timor Sea	
w	Prudhoe Bay, Alaska	
x	Saudi-Arabia	
y	OMC 4755 North Sea	medium maturity
z	OMC 3168 North Sea	low mat.
a	OMC 5217 North Sea	high mat.
b	OMC 78, Nigeria	marine oil
c	OMC 3813	landplant-derived oil
d	OMC 4677 M. East	medium mat.
e	OMC 5220 M. East	low mat.
f	OMC 5363 M. East	high mat.
g	Quiketai Seep	Turpan Basin
h	Yumen oilsand	Jiuxi Basin
i	Minghe Bridge	oilsand
k	Dorset oil sand	

Figure 56: Pc2/pc1 for New Zealand and overseas oils

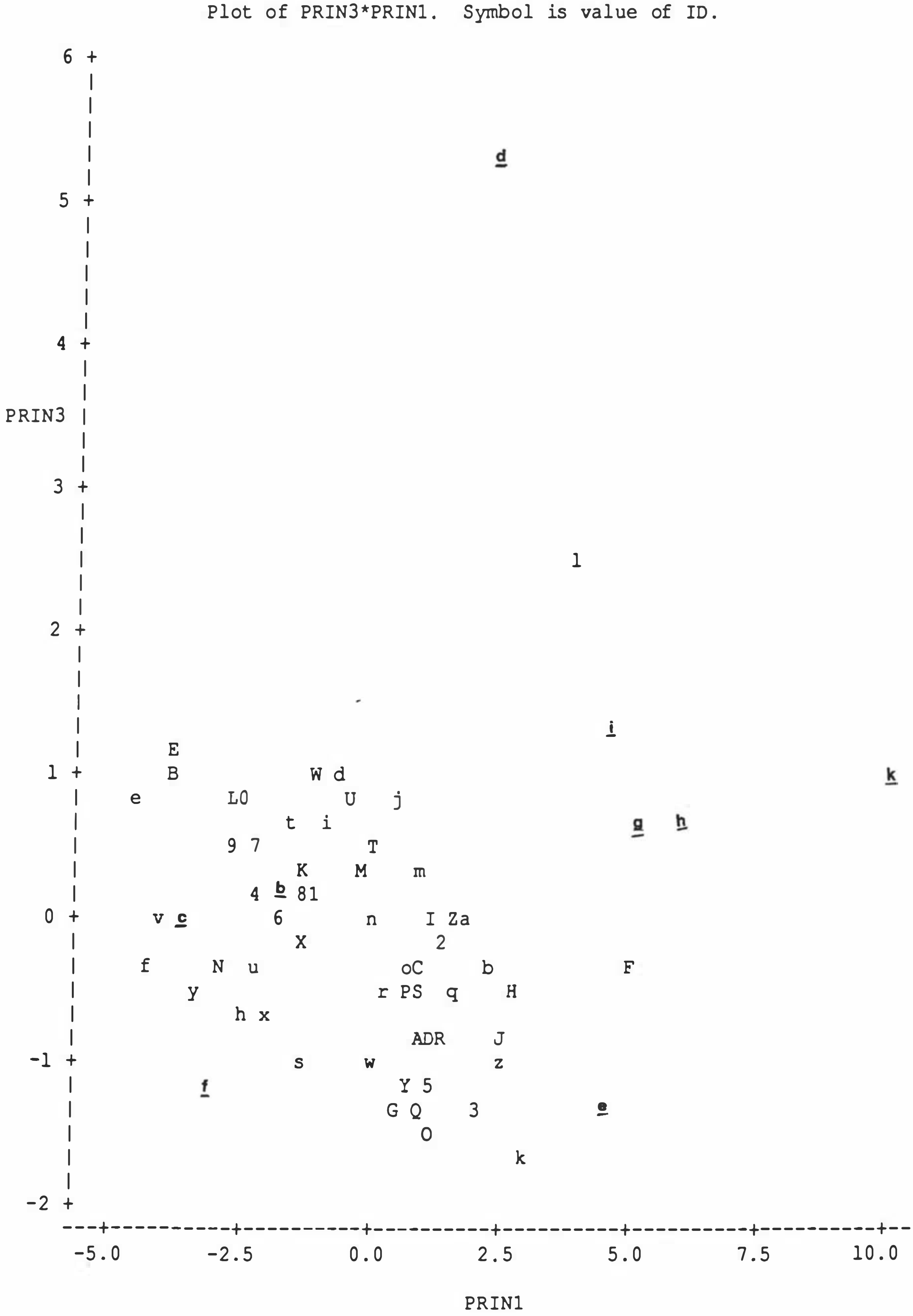


NOTE: 3 obs hidden.

LEGEND

0	Tuhua-2, B-Sand	McKee Field
1	Tuhua-2, A-Sand	McKee Field
2	Tuhua-1	McKee Field
3	Urenui-1	
4	ToeToe-1	McKee Field
5	Tariki-1	
6	ToeToe-4	McKee Field
7	ToeToe-2B	McKee Field
8	ToeToe-3	McKee Field
9	Kaimiro-1	Condensate
A	Stratford-1	
B	Pukemai-2	Condensate
C	Pouri-1	McKee Field
D	McKee-4	McKee Field
E	Tariki-1A	Condensate
F	Maui-1	
G	Maui-3	Condensate
H	Moki-1	
I	Republic-4	
J	Taranaki-5	
K	McKee-2	McKee Field
L	Blackwater	Condensate
M	Galleon-1	Condensate
N	Ahuroa-2	Condensate
O	McKee-3A	McKee Field
P	Maui-4	
Q	Kupe South-1	
R	Kapuni-1	Condensate
S	McKee-1	McKee Field
T	Waiotapu	Seep
U	Kotuku	Seep
V	Pukemai-1B	McKee Field
W	Republic-1	
X	Tuhua-2	McKee Field
Y	Stratford-1	
Z	Pukearuhe-1	
a	Moturoa	
b	Waitangi	Seep
c	Kupe-2	
d	Kupe-3	
e	Kupe-4	
f	Kupe-5	
g	Toru-1	
h	Waihapa	
i	Kora-1, DST2	
j	Kora-1, DST3	
k	Venezuela	
l	Yumen #114	lacustrine oil, Juixi B.
m	Yumen, #503	lacustrine oil, Juixi B.
n	Yumen, #502	lacustrine oil, Juixi B.
o	Yumen, #506	lacustrine oil, Juixi B.
p	Yumen, #507	lacustrine oil, Juixi B.
q	Yumen, #194	lacustrine oil, Juixi B.
r	Yumen, #68	lacustrine oil, Juixi B.
s	Hutouya, China	terr. oil
t	Toucan-1, China	terr. oil, Turpan Basin
u	Taican-1, China	terr. oil, Turpan Basin
v	Timor Sea	
w	Prudhoe Bay, Alaska	
x	Saudi-Arabia	
y	OMC 4755 North Sea	medium maturity
z	OMC 3168 North Sea	low mat.
$\underline{a}$	OMC 5217 North Sea	high mat.
$\underline{b}$	OMC 78, Nigeria	marine oil
$\underline{c}$	OMC 3813	landplant-derived oil
$\underline{d}$	OMC 4677 M. East	medium mat.
$\underline{e}$	OMC 5220 M. East	low mat.
$\underline{f}$	OMC 5363 M. East	high mat.
$\underline{g}$	Quiketai Seep	Turpan Basin
$\underline{h}$	Yumen oilsand	Jiuxi Basin
$\underline{i}$	Minghe Bridge	oilsand
$\underline{k}$	Dorset oil sand	

Figure 57: Pc3/pc1 for New Zealand and overseas oils

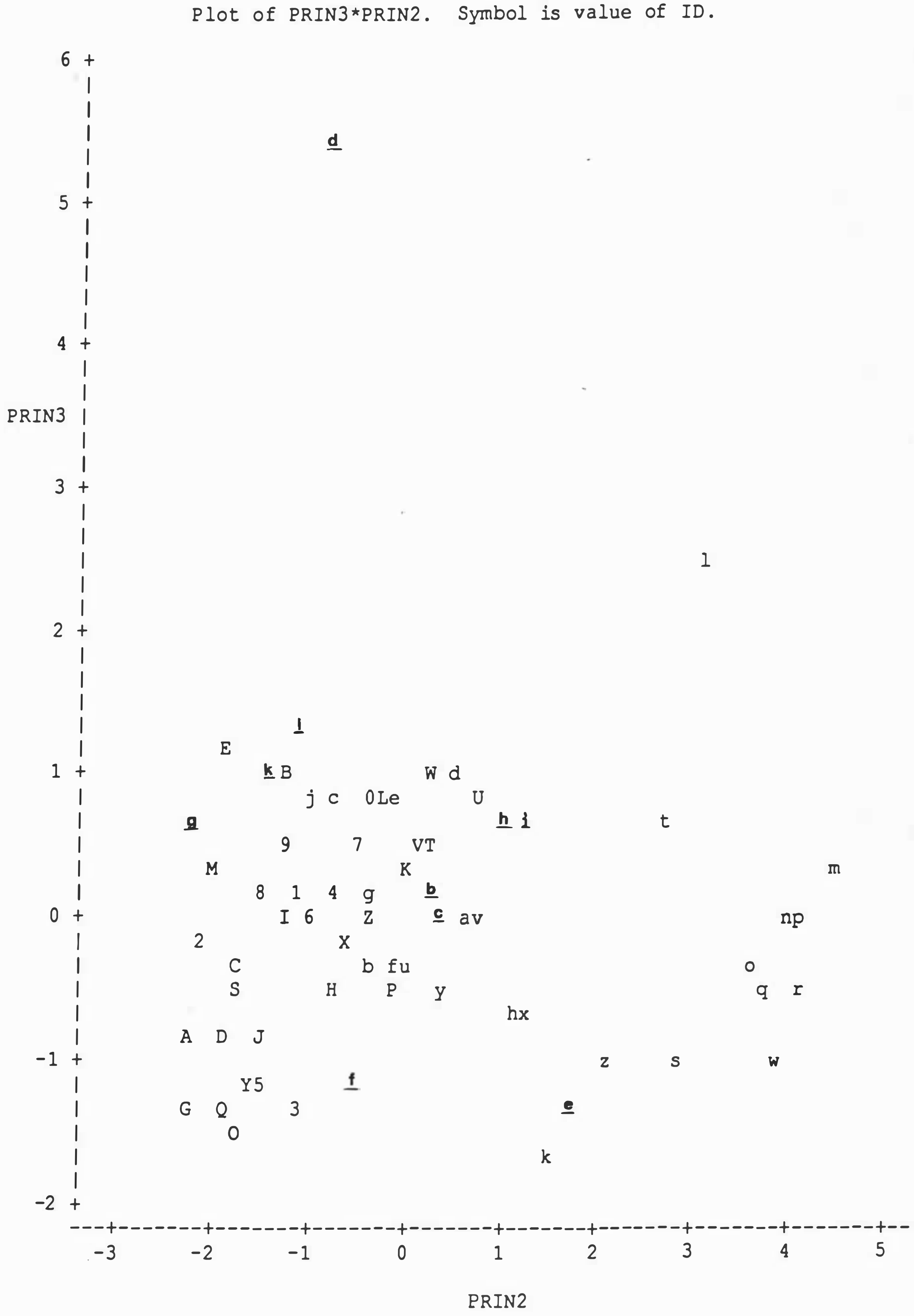


NOTE: 5 obs hidden.

LEGEND

0	Tuhua-2, B-Sand	McKee Field
1	Tuhua-2, A-Sand	McKee Field
2	Tuhua-1	McKee Field
3	Urenui-1	
4	ToeToe-1	McKee Field
5	Tariki-1	
6	ToeToe-4	McKee Field
7	ToeToe-2B	McKee Field
8	ToeToe-3	McKee Field
9	Kaimiro-1	Condensate
A	Stratford-1	
B	Pukemai-2	Condensate
C	Pouri-1	McKee Field
D	McKee-4	McKee Field
E	Tariki-1A	Condensate
F	Maui-1	
G	Maui-3	Condensate
H	Moki-1	
I	Republic-4	
J	Taranaki-5	
K	McKee-2	McKee Field
L	Blackwater	Condensate
M	Galleon-1	Condensate
N	Ahuroa-2	Condensate
O	McKee-3A	McKee Field
P	Maui-4	
Q	Kupe South-1	
R	Kapuni-1	Condensate
S	McKee-1	McKee Field
T	Waiotapu	Seep
U	Kotuku	Seep
V	Pukemai-1B	McKee Field
W	Republic-1	
X	Tuhua-2	McKee Field
Y	Stratford-1	
Z	Pukearuhe-1	
a	Moturoa	
b	Waitangi	Seep
c	Kupe-2	
d	Kupe-3	
e	Kupe-4	
f	Kupe-5	
g	Toru-1	
h	Waihapa	
i	Kora-1, DST2	
j	Kora-1, DST3	
k	Venezuela	
l	Yumen #114	lacustrine oil, Juixi B.
m	Yumen, #503	lacustrine oil, Juixi B.
n	Yumen, #502	lacustrine oil, Juixi B.
o	Yumen, #506	lacustrine oil, Juixi B.
p	Yumen, #507	lacustrine oil, Juixi B.
q	Yumen, #194	lacustrine oil, Juixi B.
r	Yumen, #68	lacustrine oil, Juixi B.
s	Hutouya, China	terr. oil
t	Toucan-1, China	terr. oil, Turpan Basin
u	Taican-1, China	terr. oil, Turpan Basi
v	Timor Sea	
w	Prudhoe Bay, Alaska	
x	Saudi-Arabia	
y	OMC 4755 North Sea	medium maturity
z	OMC 3168 North Sea	low mat.
a	OMC 5217 North Sea	high mat.
b	OMC 78, Nigeria	marine oil
c	OMC 3813	landplant-derived oil
d	OMC 4677 M. East	medium mat.
e	OMC 5220 M. East	low mat.
f	OMC 5363 M. East	high mat.
g	Quiketai Seep	Turpan Basin
h	Yumen oilsand	Jiuxi Basin
i	Minghe Bridge	oilsand
k	Dorset oil sand	

Figure 58: Pc3/pc2 for New Zealand and overseas oils

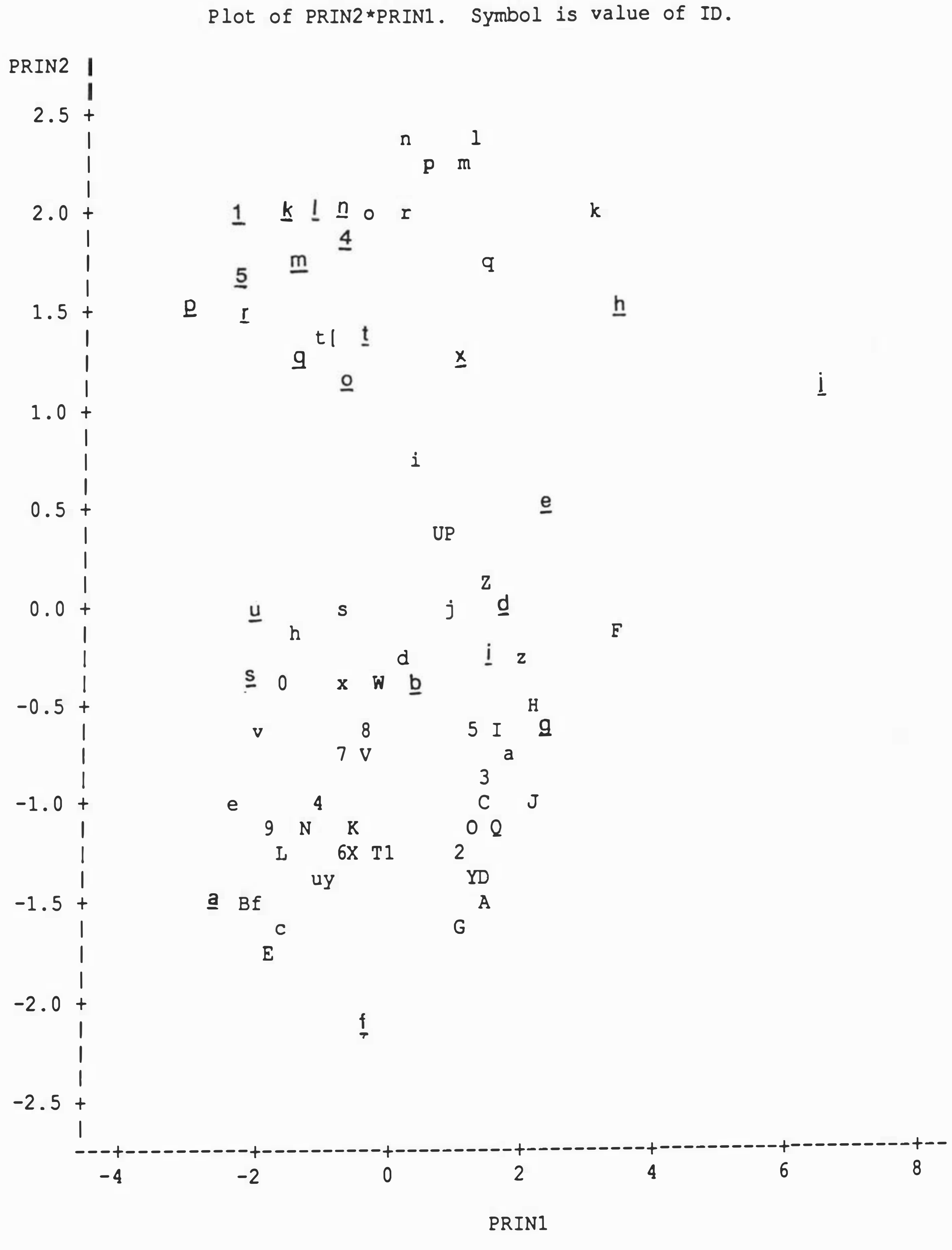


NOTE: 4 obs hidden.

LEGEND

0	Tuhua-2, B-Sand
1	Tuhua-2, A-Sand
2	Tuhua-1
3	Urenui-1
4	ToeToe-1
5	Tariki-1
6	ToeToe-4
7	ToeToe-2B
8	ToeToe-3
9	Kaimiro-1
A	Stratford-1
B	Pukemai-2
C	Pouri-1
D	McKee-4
E	Tariki-1A
F	Maui-1
G	Maui-3
H	Moki-1
I	Republic-4
J	Taranaki-5
K	McKee-2
L	Blackwater
M	Galleon-1
N	Ahuroa-2
O	McKee-3A
P	Maui-4
Q	Kupe South
R	Kapuni-1
S	McKee-1
T	Waiotapu Seep
U	Kotuku Seep
V	Pukemai-1B
W	Republic-1
X	Tuhua-2
Y	Stratford-1
Z	Pukearuhe-1
a	Moturoa
b	Waitangi Seep
c	Kupe-2
d	Kupe-3
e	Kupe-4
f	Kupe-5
g	Toru-1
h	Waihapa
i	Kora-1, DST2
j	Kora-1, DST3
k	Venezuela
l	Yumen, #114
m	Yumen, #503
n	Yumen, #502
o	Yumen, #506
p	Yumen, #507
q	Yumen, #194
r	Yumen, #68
s	Hutouya, China
t	Toucan-1, China
u	Taican-1, China
v	Timor Sea
w	Prudhoe Bay, Alaska
x	Saudi-Arabia
y	OMC 4755, North Sea, med mat.
z	OMC 3168 North Sea, low mat.
a̲	OMC 5217 North Sea, high mat.
b̲	OMC 78, Nigeria, marine
c̲	OMC 3813, Nigeria, landplant
d̲	OMC 4677, Middle East, med. mat.
e̲	OMC 5220, M.E., low mat.
f̲	OMC 5363, M.E., high mat.
g̲	Quiketai Seep, China
h̲	Yumen, oilsand
i̲	Minghe Bridge, oilsand
j̲	Dorset oil sand
k̲	154627 A, Los Angeles Basin
l̲	154627 F, LA Basin
m̲	56323, North Sea
n̲	22970, Williston Basin
o̲	54051 A, North Sea
p̲	41054, Gulf of Mexico
q̲	154627 B, LA Basin
r̲	22971, Williston B.
s̲	51577, Alberta B., Canada
t̲	22966, Williston Basin
u̲	48101, Alberta B., Canada
v̲	19126, Uinta Basin, Utah
e̲	154627 H, LA Basin
x̲	19125, Uinta B., Utah
y̲	41056, Gulf of Mexico
z̲	154627 I, LA Basin
1̲	154627 K, LA Basin
2̲	22974, Williston Basin
3̲	21850, Uinta B., Utah
4̲	154627 D, LA Basin
5̲	154627 E, LA Basin

Figure 59: Pc2/pc1 for all oil samples (6 trace elements)



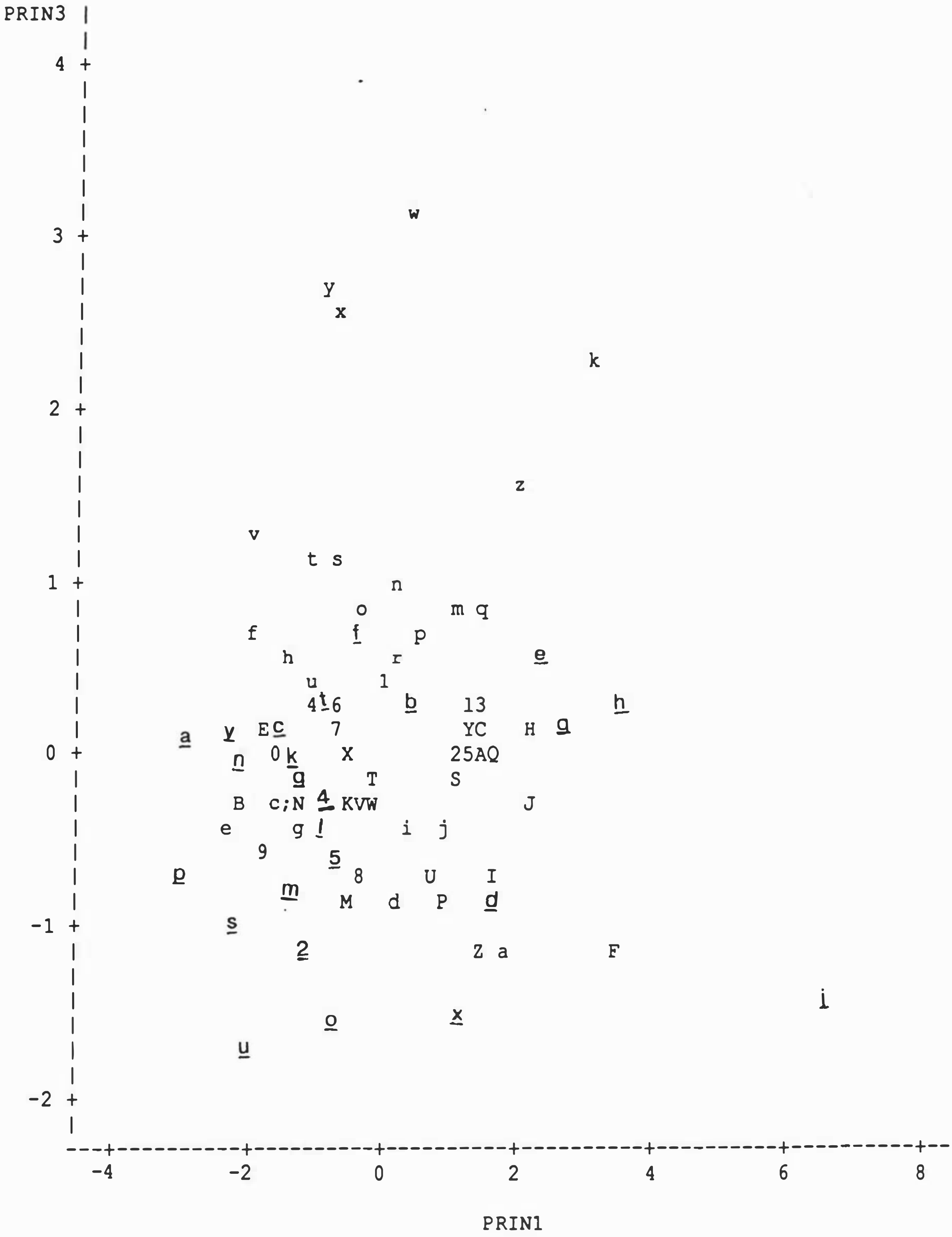
NOTE: 3 obs had missing values. 8 obs hidden.

LEGEND

0	Tuhua-2, B-Sand
1	Tuhua-2, A-Sand
2	Tuhua-1
3	Urenui-1
4	ToeToe-1
5	Tariki-1
6	ToeToe-4
7	ToeToe-2B
8	ToeToe-3
9	Kaimiro-1
A	Stratford-1
B	Pukemai-2
C	Pouri-1
D	McKee-4
E	Tariki-1A
F	Maui-1
G	Maui-3
H	Moki-1
I	Republic-4
J	Taranaki-5
K	McKee-2
L	Blackwater
M	Galleon-1
N	Ahuroa-2
O	McKee-3A
P	Maui-4
Q	Kupe South
R	Kapuni-1
S	McKee-1
T	Waiotapu Seep
U	Kotuku Seep
V	Pukemai-1B
W	Republic-1
X	Tuhua-2
Y	Stratford-1
Z	Pukearuhe-1
a	Moturoa
b	Waitangi Seep
c	Kupe-2
d	Kupe-3
e	Kupe-4
f	Kupe-5
g	Toru-1
h	Waihapa
i	Kora-1, DST2
j	Kora-1, DST3
k	Venezuela
l	Yumen, #114
m	Yumen, #503
n	Yumen, #502
o	Yumen, #506
p	Yumen, #507
q	Yumen, #194
r	Yumen, #68
s	Hutouya, China
t	Toucan-1, China
u	Taican-1, China
v	Timor Sea
w	Prudhoe Bay, Alaska
x	Saudi-Arabia
y	OMC 4755, North Sea, med mat.
z	OMC 3168 North Sea, low mat.
a̲	OMC 5217 North Sea, high mat.
b̲	OMC 78, Nigeria, marine
c̲	OMC 3813, Nigeria, landplant
d̲	OMC 4677, Middle East, med. mat.
e̲	OMC 5220, M.E., low mat.
f̲	OMC 5363, M.E., high mat.
g̲	Quiketai Seep, China
h̲	Yumen, oilsand
i̲	Minghe Bridge, oilsand
j̲	Dorset oil sand
k̲	154627 A, Los Angeles Basin
l̲	154627 F, LA Basin
m̲	56323, North Sea
n̲	22970, Williston Basin
o̲	54051 A, North Sea
p̲	41054, Gulf of Mexico
q̲	154627 B, LA Basin
r̲	22971, Williston B.
s̲	51577, Alberta B., Canada
t̲	22966, Williston Basin
u̲	48101, Alberta B., Canada
v̲	19126, Uinta Basin, Utah
e̲	154627 H, LA Basin
x̲	19125, Uinta B., Utah
y̲	41056, Gulf of Mexico
z̲	154627 I, LA Basin
1̲	154627 K, LA Basin
2̲	22974, Williston Basin
3̲	21850, Uinta B., Utah
4̲	154627 D, LA Basin
5̲	154627 E, LA Basin

Figure 60: Pc3/pc1 for all oil samples (6 trace elements)

Plot of PRIN3*PRIN1. Symbol is value of ID.



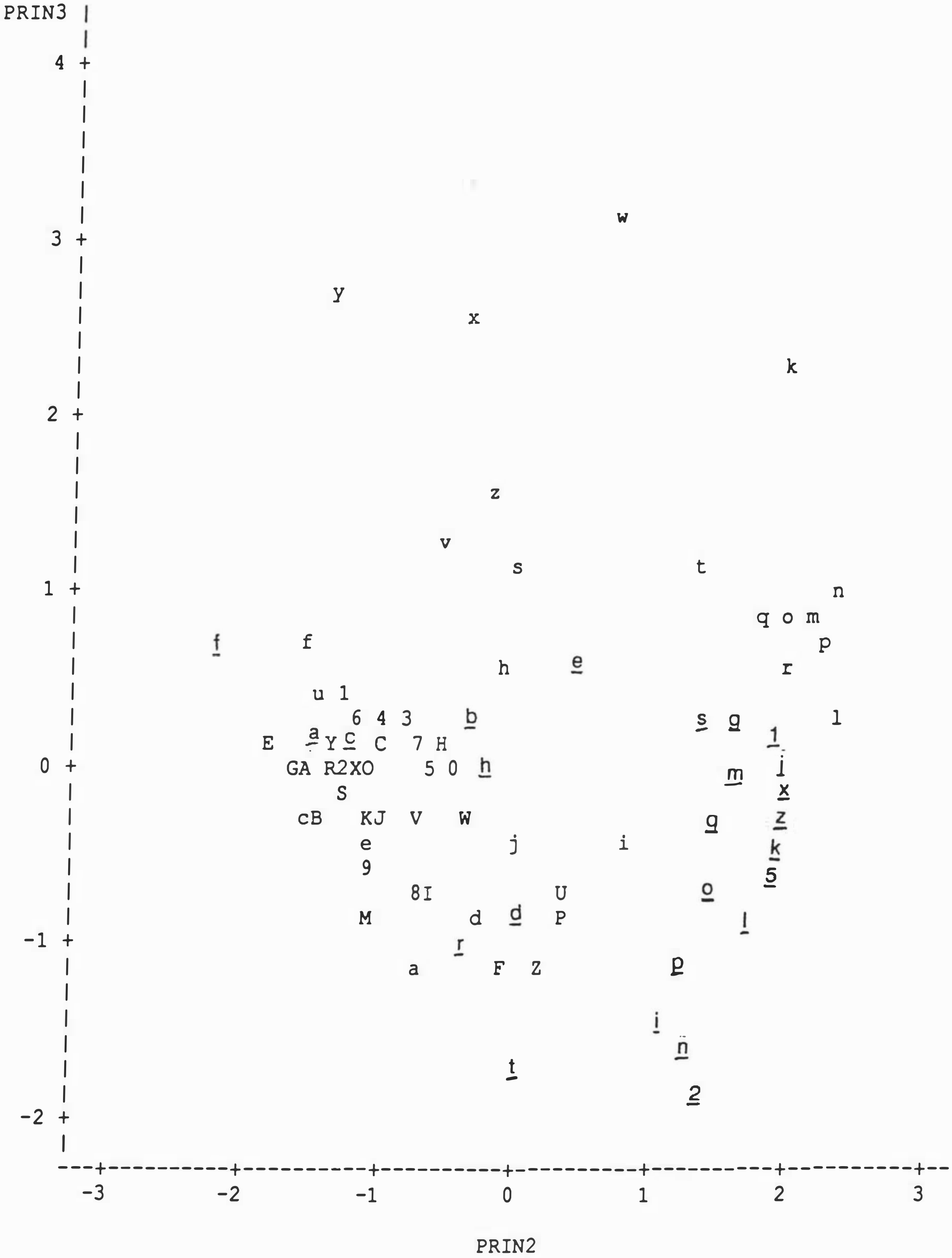
NOTE: 3 obs had missing values. 9 obs hidden.

LEGEND

0	Tuhua-2, B-Sand
1	Tuhua-2, A-Sand
2	Tuhua-1
3	Urenui-1
4	ToeToe-1
5	Tariki-1
6	ToeToe-4
7	ToeToe-2B
8	ToeToe-3
9	Kaimiro-1
A	Stratford-1
B	Pukemai-2
C	Pouri-1
D	McKee-4
E	Tariki-1A
F	Maui-1
G	Maui-3
H	Moki-1
I	Republic-4
J	Taranaki-5
K	McKee-2
L	Blackwater
M	Galleon-1
N	Ahuroa-2
O	McKee-3A
P	Maui-4
Q	Kupe South
R	Kapuni-1
S	McKee-1
T	Waiotapu Seep
U	Kotuku Seep
V	Pukemai-1B
W	Republic-1
X	Tuhua-2
Y	Stratford-1
Z	Pukearuhe-1
a	Moturoa
b	Waitangi Seep
c	Kupe-2
d	Kupe-3
e	Kupe-4
f	Kupe-5
g	Toru-1
h	Waihapa
i	Kora-1, DST2
j	Kora-1, DST3
k	Venezuela
l	Yumen, #114
m	Yumen, #503
n	Yumen, #502
o	Yumen, #506
p	Yumen, #507
q	Yumen, #194
r	Yumen, #68
s	Hutouya, China
t	Toucan-1, China
u	Taican-1, China
v	Timor Sea
w	Prudhoe Bay, Alaska
x	Saudi-Arabia
y	OMC 4755, North Sea, med mat.
z	OMC 3168 North Sea, low mat.
$\underline{a}$	OMC 5217 North Sea, high mat.
$\underline{b}$	OMC 78, Nigeria, marine
$\underline{c}$	OMC 3813, Nigeria, landplant
$\underline{d}$	OMC 4677, Middle East, med. mat.
$\underline{e}$	OMC 5220, M.E., low mat.
$\underline{f}$	OMC 5363, M.E., high mat.
$\underline{g}$	Quiketai Seep, China
$\underline{h}$	Yumen, oilsand
$\underline{i}$	Minghe Bridge, oilsand
$\underline{j}$	Dorset oil sand
$\underline{k}$	154627 A, Los Angeles Basin
$\underline{l}$	154627 F, LA Basin
$\underline{m}$	56323, North Sea
$\underline{n}$	22970, Williston Basin
$\underline{o}$	54051 A, North Sea
$\underline{p}$	41054, Gulf of Mexico
$\underline{q}$	154627 B, LA Basin
$\underline{r}$	22971, Williston B.
$\underline{s}$	51577, Alberta B., Canada
$\underline{t}$	22966, Williston Basin
$\underline{u}$	48101, Alberta B., Canada
$\underline{v}$	19126, Uinta Basin, Utah
$\underline{e}$	154627 H, LA Basin
$\underline{x}$	19125, Uinta B., Utah
$\underline{y}$	41056, Gulf of Mexico
$\underline{z}$	154627 I, LA Basin
$\underline{1}$	154627 K, LA Basin
$\underline{2}$	22974, Williston Basin
$\underline{3}$	21850, Uinta B., Utah
$\underline{4}$	154627 D, LA Basin
$\underline{5}$	154627 E, LA Basin

Figure 61: Pc3/pc2 for all oil samples (6 trace elements)

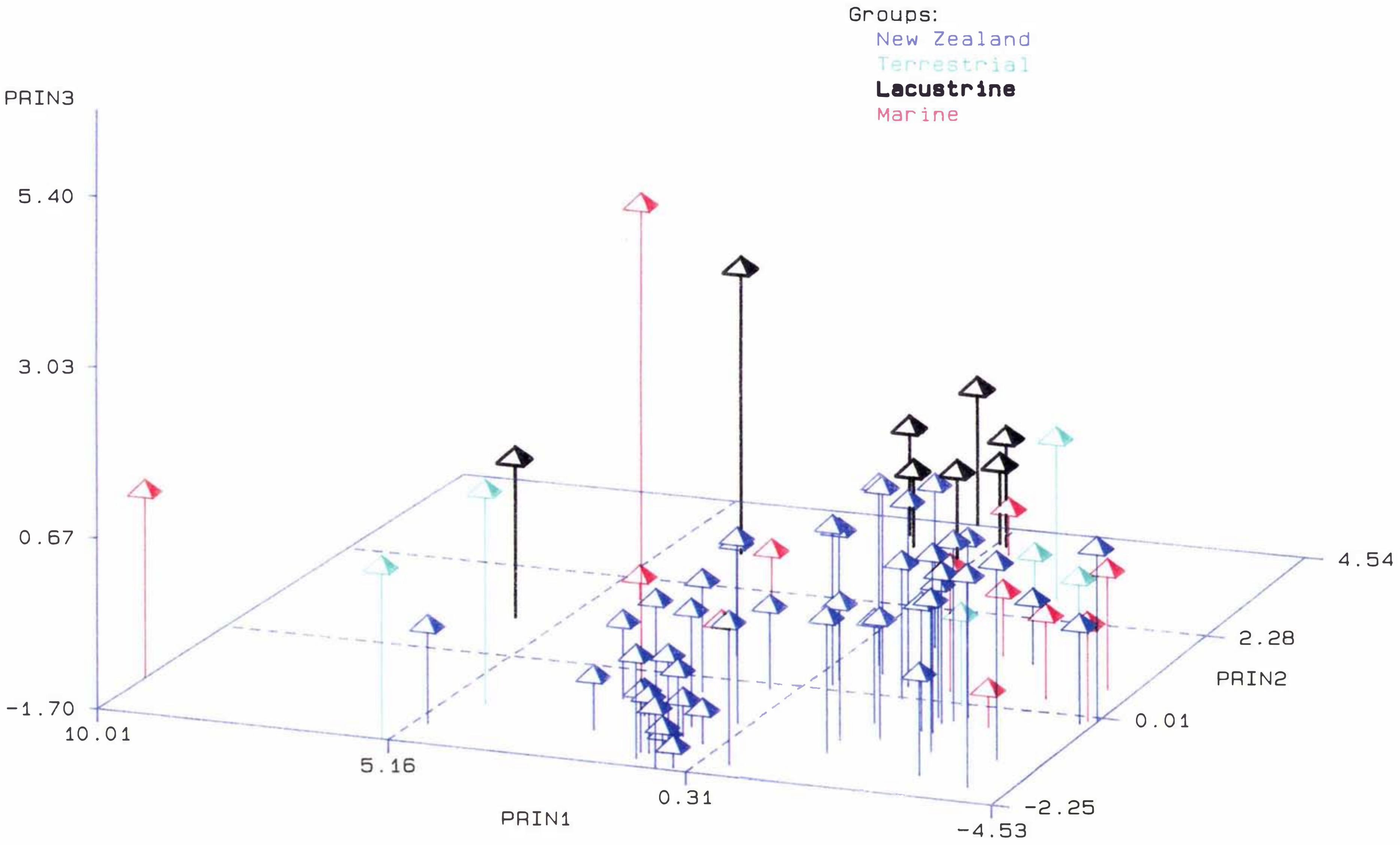
Plot of PRIN3*PRIN2. Symbol is value of ID.



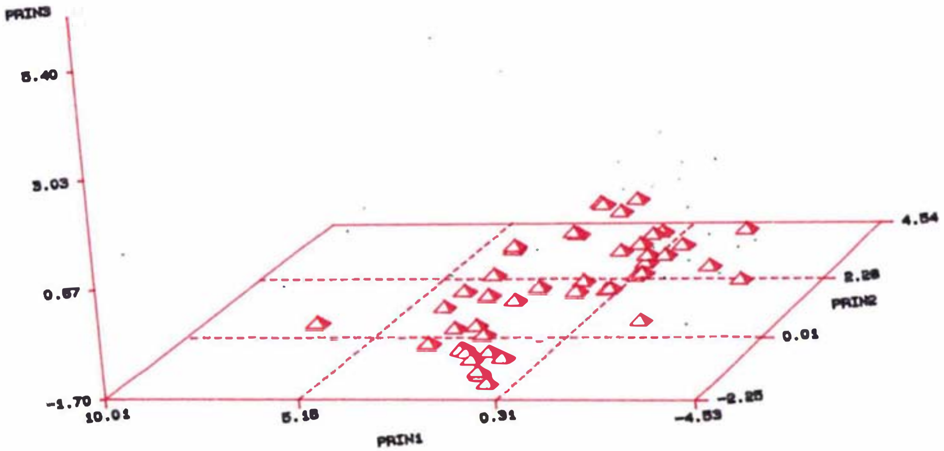
NOTE: 3 obs had missing values. 9 obs hidden.

Figures 62 and 62a: Three dimensional graphs of principal components for New Zealand and overseas oils

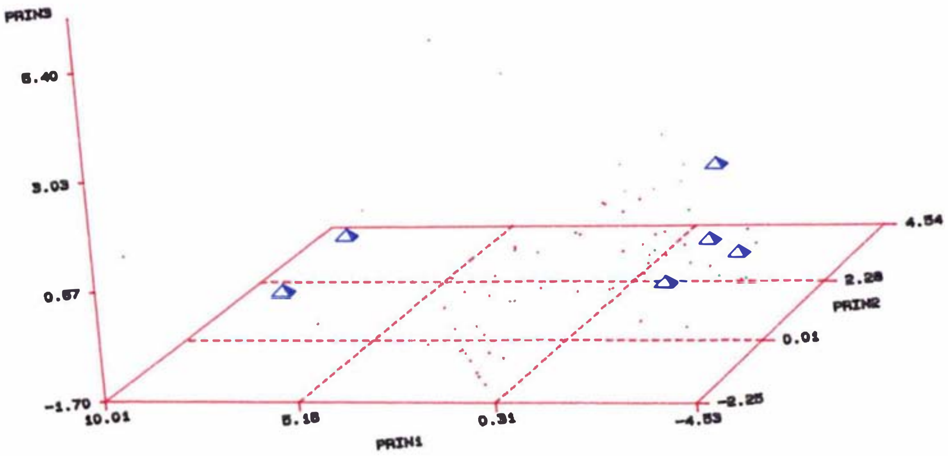
ALL OILS – ALL GROUPS



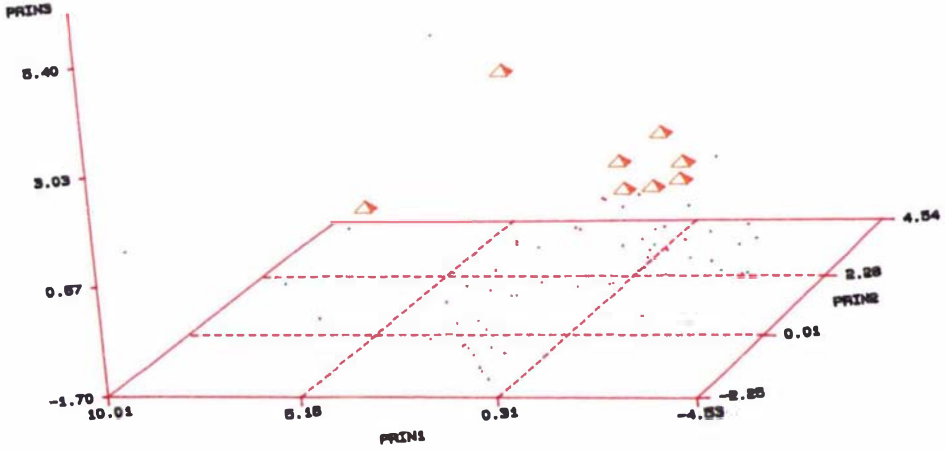
ALL OILS – NEW ZEALAND



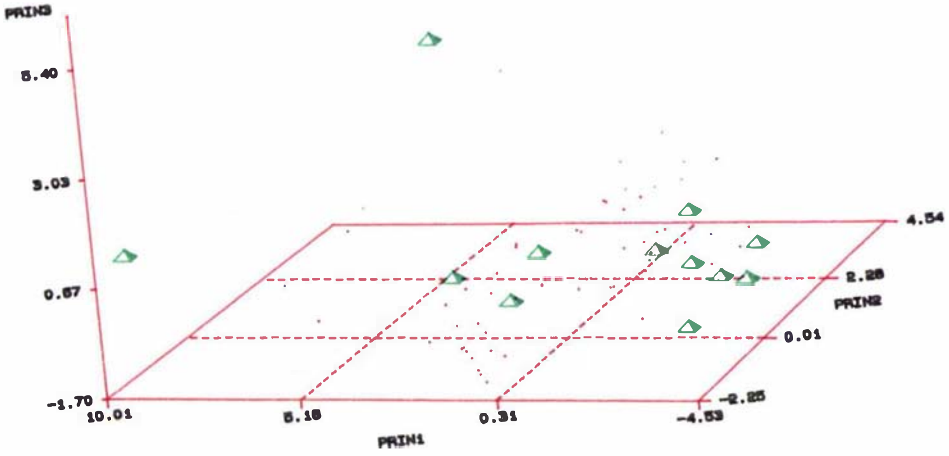
ALL OILS – TERRESTRIAL



ALL OILS – LACUSTRINE

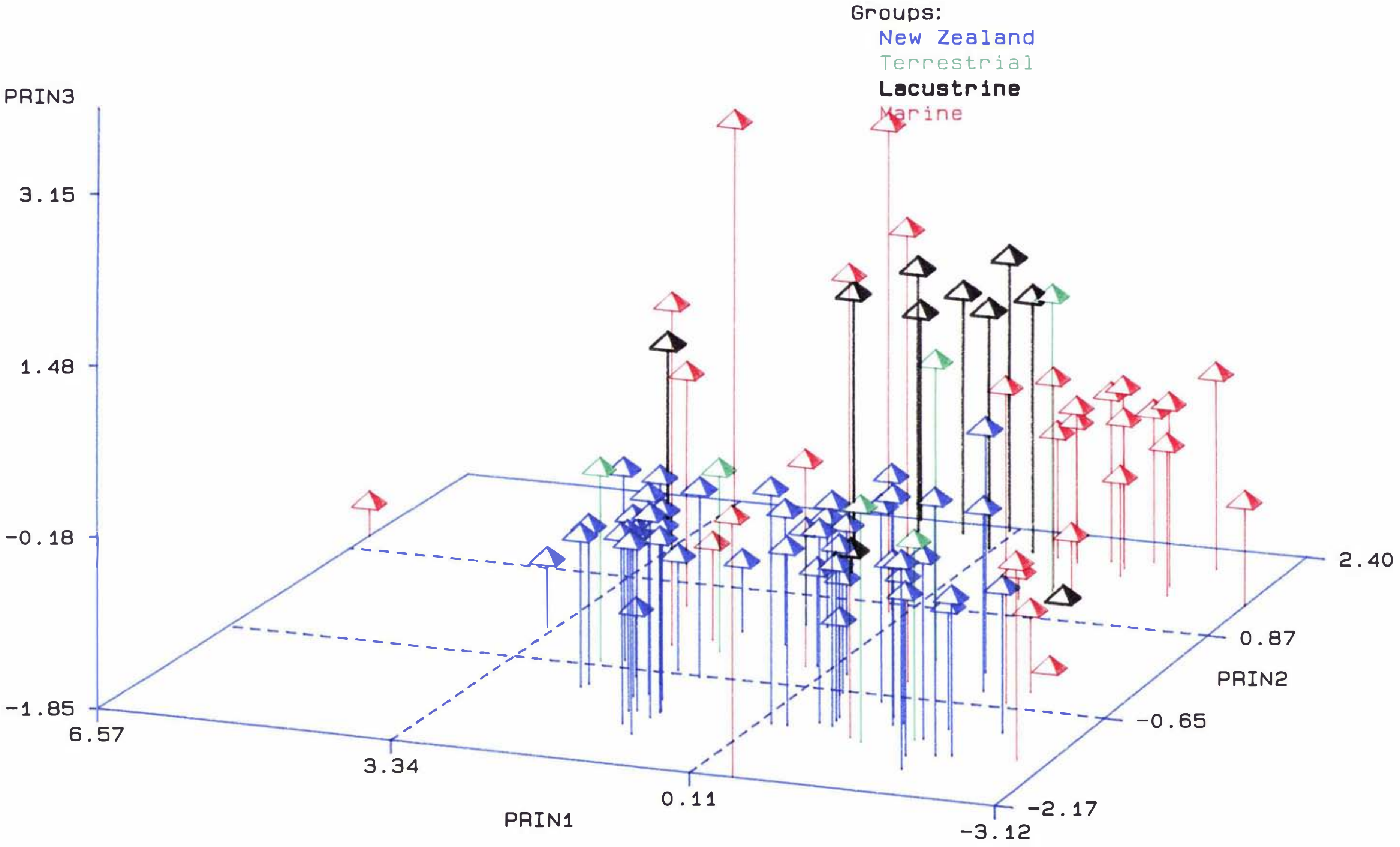


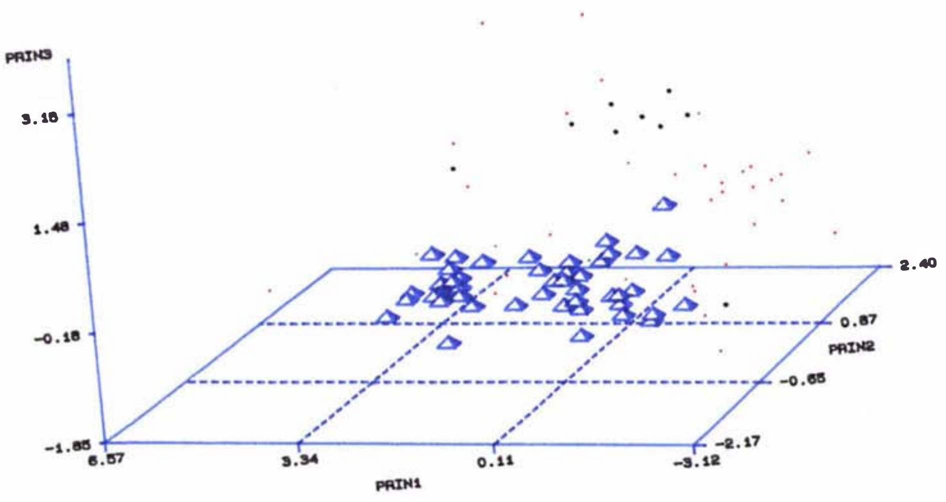
ALL OILS – MARINE



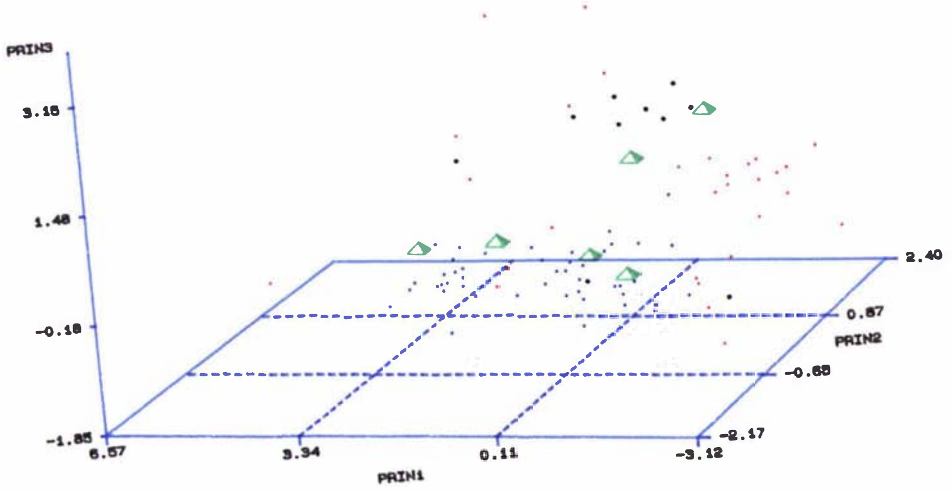
Figures 63 and 63a: Three dimensional graphs of principal components for New Zealand and overseas oils (6 trace elements, 122 samples)

ALUMAR – ALL GROUPS

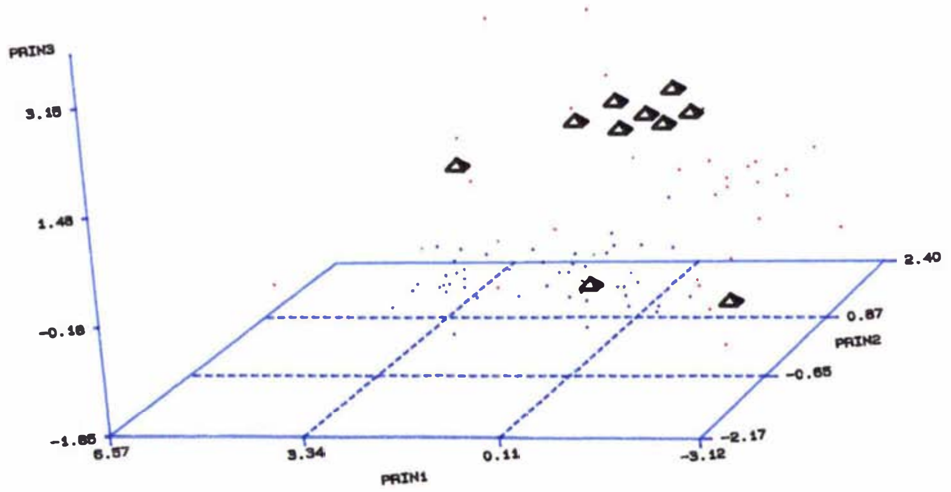




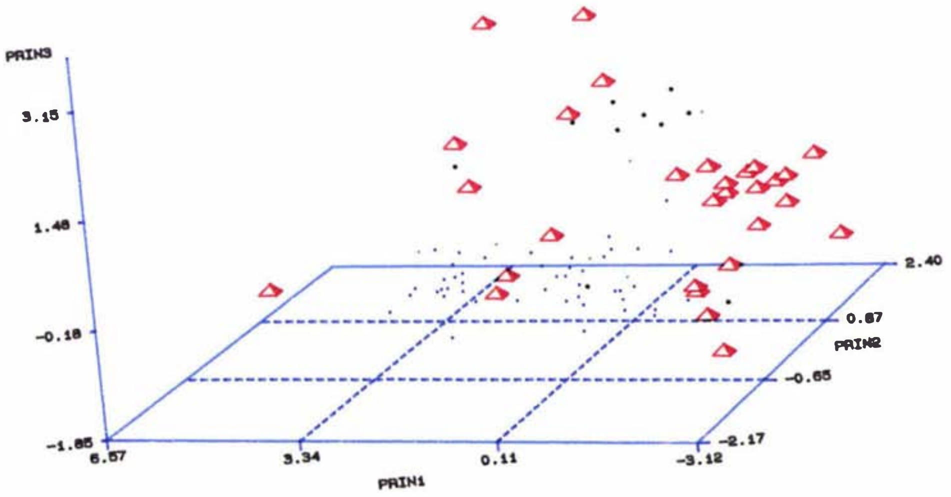
ALLMAR – NEW ZEALAND



ALLMAR – TERRESTRIAL



ALLMAR – LACUSTRINE



ALLMAR – MARINE

the relatively low concentrations found in the New Zealand samples. Another possibility is mineral matter contributing to the total trace element content in New Zealand oils, which is responsible for the large variations in concentrations observed in the New Zealand samples.

4.5.3 New Zealand oils and extracts

Plots of New Zealand oils and bitumen are more useful than total trace element concentrations, as PCA is based on the variations of element contents. The Toko-1 extracts in plots of pc1/pc2 and pc2/pc3 (Figure 64 and Figure 65) lie distinctly separate from the rest of the extracts and oils. The bitumen of the Maui-4 well cutting is not located near the Maui-4 oil and usually lies slightly separate from other extracts. As PCA is based on variations of trace element contents, oils and their source rock should show similar patterns. As the Maui-4 extract and coal are related, but lie separate on the plots, the element concentrations in the oil must have been affected during migration or in the reservoir.

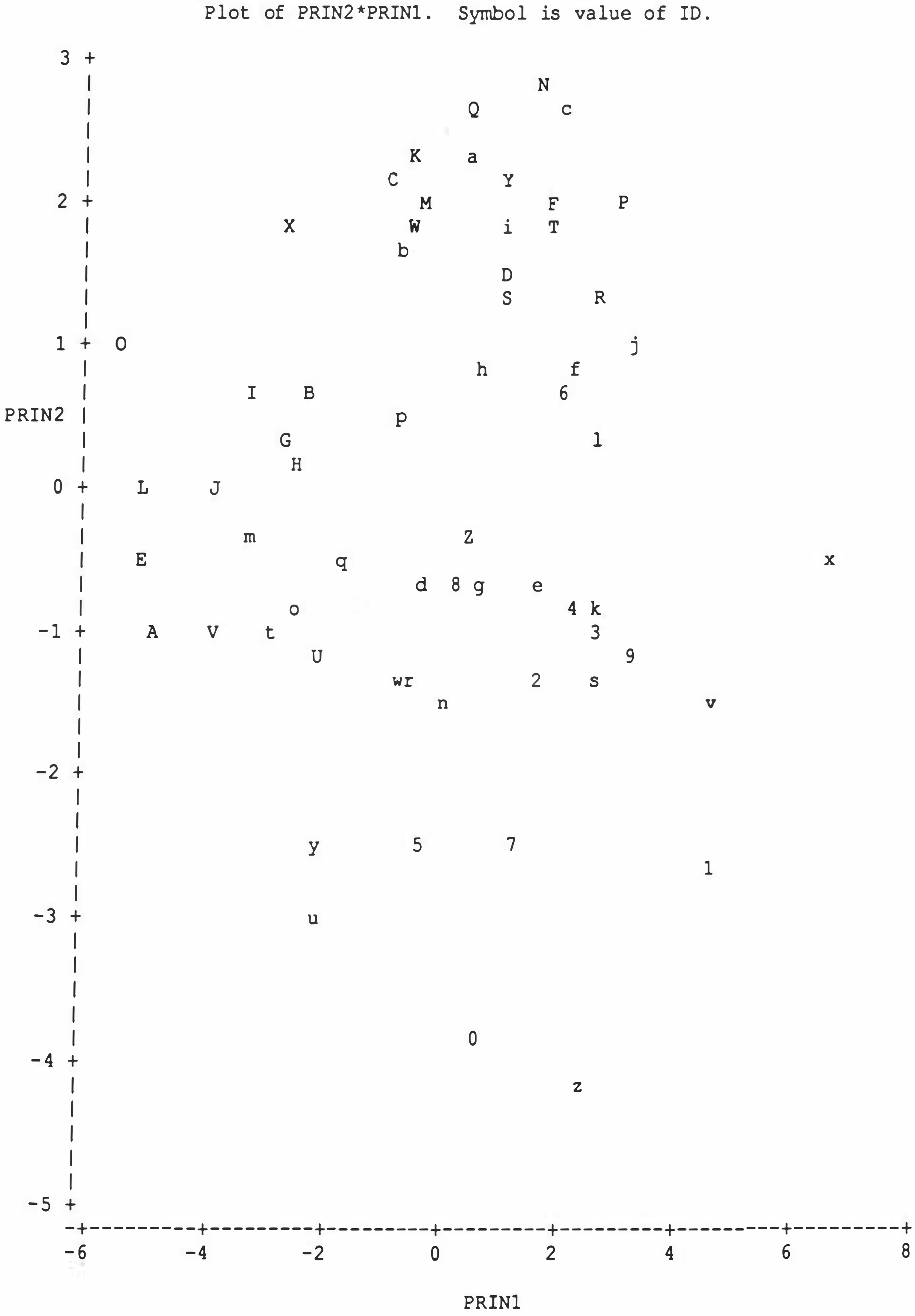
The extracts of pyrolysed coal are distributed close to or amongst the oils, showing that the hydrocarbons produced during pyrolysis might be related to the oils. No clear connection is possible as the oils are spread very widely throughout the graph. Usually, hydrocarbons produced during pyrolysis of possible source rocks resemble oils and condensates much closer than normal extracts (*Filby, pers. comm.*).

No definite connection between oils and coal extracts is possible as variations are too great and similarities in trace element behaviour are not consistent. The extracts of pyrolysed rocks seem to be more closely related to oils than other extracts from well cuttings or coals. Maui-4 oil and extract cannot be linked from their trace element contents alone. The solvent used in the extractions has a big influence on the final result, as is shown by the differences observed in the plots between bitumen extracted by chloroform/methanol and toluene/methanol.

LEGEND

A	Tuhua-2, B-Sand
B	Tuhua-2, A-Sand
C	Tuhua-1
D	Urenui-1
E	ToeToe-1
F	Tariki-1
G	ToeToe-4
H	ToeToe-2B
I	ToeToe-3
J	Kaimiro-1
K	Stratford-1
L	Pukemai-2
M	Pouri-1
N	McKee-4
O	Tariki-1A
P	Maui-1
Q	Maui-3
R	Moki-1
S	Republic-4
T	Taranaki-5
U	McKee-2
V	Blackwater
W	Galleon-1
X	Ahuroa-2
Y	McKee-3A
Z	Maui-4
a	Kupe South
b	Kapuni-1
c	McKee-1
d	Waiotapu Seep
e	Kotuku Seep
f	Pukemai-1B
g	Republic-1
h	Tuhua-2
i	Stratford-1
j	Pukearuhe-1
k	Moturoa
l	Waitangi Seep
m	Kupe-2
n	Kupe-3
o	Kupe-4
p	Kupe-5
q	Toru-1
r	Waihapa
s	Kora-1, DST2
t	Kora-1, DST3
u	Mangaraukau coal extract
v	Wairoa coal extract
w	Puponga coal extractex
x	North Cape coal extract
y	Maui-4 coal extract
z	Toko-1, A extr.
0	Toko-1, B extr.
1	Toko-1, C extr.
2	Wairoa coal, extr. with to.l/meth.
3	Wairoa coal, after hydr. pyrolysis
4	Mangarakau coal, extr. with tol./meth.
5	Mangarakau coal, aftr hydr. pyrolysis
6	Puponga coal, extr. with tol./meth.
7	Puponga coal, after hydr. pyrolysis
8	North Cape coal, extr. with tol./meth.
9	North Cape coal, after hydr. pyrolysis

Figure 64: Pc2/pc1 for New Zealand oils and bitumen

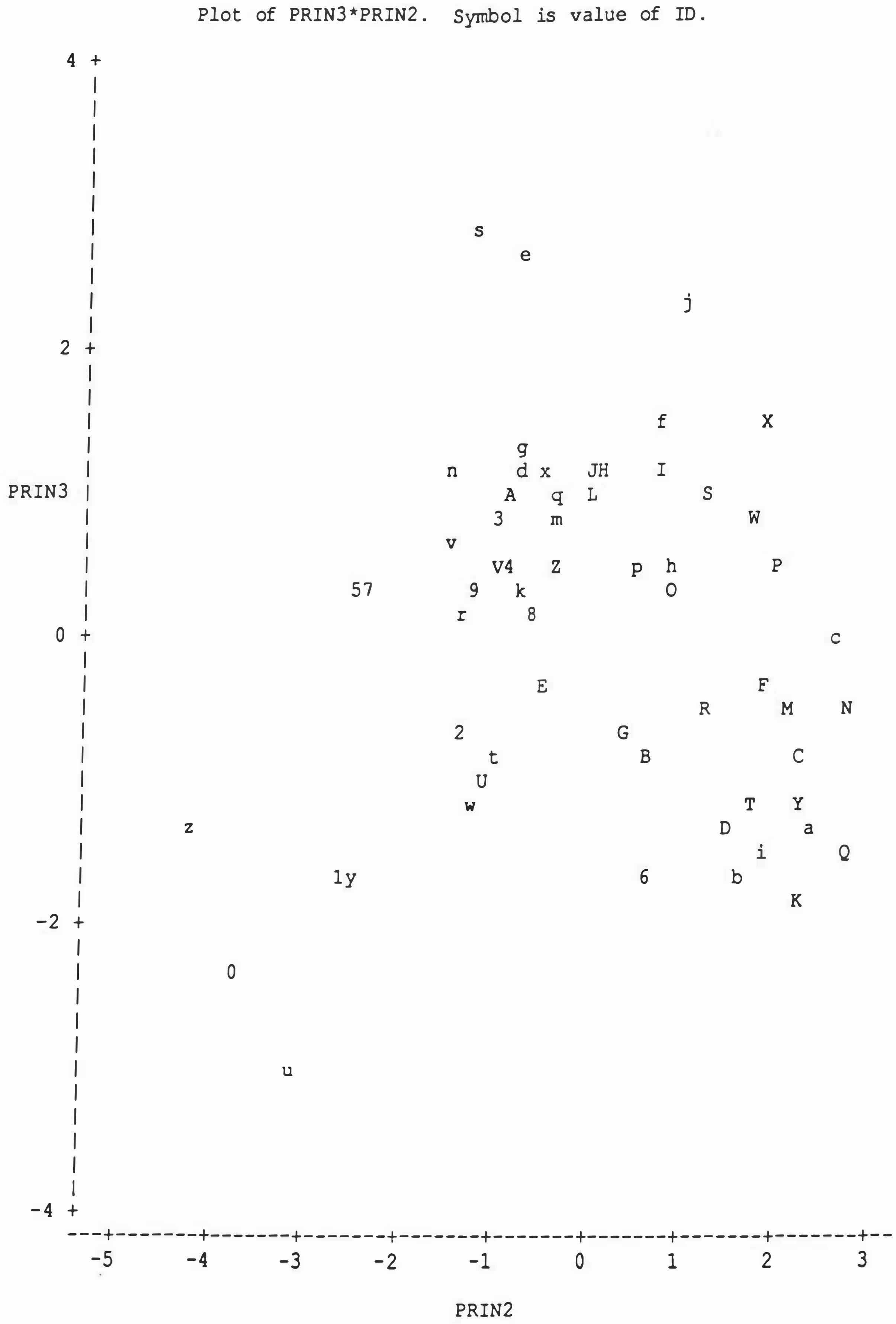


LEGEND

A	Tuhua-2, B-Sand
B	Tuhua-2, A-Sand
C	Tuhua-1
D	Urenui-1
E	ToeToe-1
F	Tariki-1
G	ToeToe-4
H	ToeToe-2B
I	ToeToe-3
J	Kaimiro-1
K	Stratford-1
L	Pukemai-2
M	Pouri-1
N	McKee-4
O	Tariki-1A
P	Maui-1
Q	Maui-3
R	Moki-1
S	Republic-4
T	Taranaki-5
U	McKee-2
V	Blackwater
W	Galleon-1
X	Ahuroa-2
Y	McKee-3A
Z	Maui-4
a	Kupe South
b	Kapuni-1
c	McKee-1
d	Waiotapu Seep
e	Kotuku Seep
f	Pukemai-1B
g	Republic-1
h	Tuhua-2
i	Stratford-1
j	Pukearuhe-1
k	Moturoa
l	Waitangi Seep
m	Kupe-2
n	Kupe-3
o	Kupe-4
p	Kupe-5
q	Toru-1
r	Waihapa
s	Kora-1, DST2
t	Kora-1, DST3

u	Mangaraukau coal extract
v	Wairoa coal extract
w	Puponga coal extractex
x	North Cape coal extract
y	Maui-4 coal extract
z	Toko-1, A extr.
0	Toko-1, B extr.
1	Toko-1, C extr.
2	Wairoa coal, extr. with to.l/meth.
3	Wairoa coal, after hydr. pyrolysis
4	Mangarakau coal, extr. with tol./meth.
5	Mangarakau coal, aftr hydr. pyrolysis
6	Puponga coal, extr. with tol./meth.
7	Puponga coal, after hydr. pyrolysis
8	North Cape coal, extr. with tol./meth.
9	North Cape coal, after hydr. pyrolysis

Figure 65: Pc3/pc2 for New Zealand oils and bitumen



NOTE: 2 obs hidden.

Principal components analysis can separate terrestrial, lacustrine and marine-sourced oils, based on differences in trace element concentrations. No further information about the relation of Taranaki oils could be obtained as the oils are spread over a wide range and no definite clusters could be identified. Seep oils and oils with marine influence lie separate from other Taranaki oils.

4.6 ASPHALTENES

Asphaltenes are polar components that are able to bind trace elements to their heteroatoms and are usually enriched in certain trace elements like Co, Ni and Zn. *Hirner (1987)* used trace elements in asphaltenes and maltenes[1] to group South German oils into related families. Trace elements found in this polar fraction are probably derived from the original source rock and related oils should show similar trace element distribution in asphaltenes.

New Zealand oils contain only very small amounts of asphaltenes, when compared to marine oils. Element concentrations in asphaltenes are listed in Appendix H. Most elements are enriched in the asphaltene fraction, with Co and Ni showing the highest enrichment factors in New Zealand oils, indicating that these elements are mainly bound to the organic fraction. Maui-4, Kora-1 and Pukearuhe-1 oils contain a higher proportion of elements in their asphaltene fractions, as their enrichment factors for most elements are consistently higher than in other samples. In a graph of Co versus Ni and Mn versus Fe concentrations for New Zealand asphaltenes (Figures 66 and 67), the different trace element concentrations in Kotuku Seep oil, Maui-1, Maui-4 and the Kora-1 asphaltenes are clearly visible. The different concentrations in the Kora-1 asphaltenes probably reflect the distinct marine influence, whereas the higher trace element content in the Kotuku Seep asophaltenes might be due to its different source rock in the westland Basin. Maui-1 and Maui-4 are mature oils and biomarker and isotope studies showed that these two oils are slightly different, with the Maui-1 oil possibly derived from a source rock with more marine influence (*Robertson Research 1984).* The two Kora-1 asphaltene samples show almost identical Co and Ni concentrations, indicating that they are obviously closely related. Oils

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[1] maltenes: fraction of oil without asphaltenes

from shallow reservoirs, such as Republic-1, Republic-4 and Taranaki-5, form a tight cluster, with the Pukearuhe-1 and Waitangi seep sample in the same group.

The Co content in asphaltenes seems to vary more than the Ni concentration. The Waiotapu Seep is located at the lower end of the scale in both plots (66 and 67). The McKee samples can be found in one large group, together with Urenui, Kupe and Moki samples. In both graphs, all seep oils, Maui-1, Maui-4 and both Kora oil samples lie separate from the rest of the oils.

Elements in oils that are highly correlated and associated with clays, are only slightly enriched in the asphaltene fraction of oils from onshore Taranaki (e.g. McKee Field), indicating that only small proportions of these elements are bound to the polar components and mainly occur in other fractions of the oil. Small amounts of very finely dispersed clay with grain size small enough to pass through filter paper might be still present in the asphaltene fraction. The Maui-4 and Kora-1 asphaltenes show enrichments of all elements determined by INAA, which makes these oils different to all others in their enrichment pattern.

Recent research has shown that clay minerals might play an important part in the formation of oils, as they can help to crack hydrocarbons in the kerogen by acting as catalysts *(Kaplan 1992)*. The interaction of clay with organic material can control the chemical nature of the produced hydrocarbons, as the retention of asphaltenes and bitumen by clays could lead to the formation of lighter hydrocarbons at greater depths.

Hirner (1987) used trace element concentrations (Co, I, Ni, V, Zn) in asphaltenes and maltenes to discriminate between oils of different basins. A graph of Co in maltenes versus the Co content in asphaltenes (Figure 68) allows a limited discrimination of New Zealanmd oils. A weak correlation between the Co content in asphaltenes and maltenes can be observed. Oils with high element content in the asphaltene fraction show high element concentration in the maltene fraction. Offshore oils, Maui-1, Maui-4, Kora-1 and Kupe are clearly separated from other onshore Taranaki oils with the exception of Kupe-3, Moki and Pukearuhe. Moki-1 and Kupe-3 samples are almost identical in their distribution of Co in asphaltenes and maltenes. The Waiotapu and Waitangi Seep oils lie at the lower end of the scale with the Kupe-2 and Toru sample. Kupe-2 and Toru-1 come from the same offshore area. A graph of Ni (maltenes) versus Ni (asphaltenes) (Figure 69) does not show any distinct differences in trace element content for New Zealand oils. The Kora-1 samples contain similar amounts of Ni in asphaltenes, but the Ni concentration in maltenes is different. No further subgroups are visible, indicating that the oils might be derived from the same or very similar source rocks. The loss of asphaltenes during migration could alter the trace element concentration, but trace element ratios should not be affected, if the oils originated from the same source (*Al-Sharistani* and *Al-Atyia 1979).*

Asphaltenes of overseas oils show similar enrichment patterns and a graph of Co versus Ni (Figure 70) shows that marine oils generally contain more Ni in their asphaltene fraction than terrestrial-derived oils. Asphaltenes precipitated from Australian oils contain Co and Ni in amounts very similar to New Zealand oils. The Ni content in asphaltenes from marine oil samples is very similar, whereas Co varies more widely.

The analysis of the asphaltene fractions in New Zealand oils shows that many elements are enriched in the polar fractions. Graphs allow for a separation of Kora-1, Maui and Kotuku seep oils. McKee samples are distributed in a relatively area of the graph and shallow oil samples (Republic and Taranaki) contain very similar amounts of trace elements in their asphaltene fraction. This could indicate an identical or very similar source rock. Further discrimination could be achieved by analysing the trace element compounds in asphaltenes, e.g. porphyrin complexes, to establish the amount of trace elements bound in organic complexes. *Filby (1975)* suggested that the amount and type of porphyrin complexes could supply information about the relationship of oils. As asphaltene and resin fractions constitute only a minor part of the New Zealand oils, this was not a possibility.

Figure 66: Cobalt (ng/g) versus Ni (µg/g) for asphaltenes

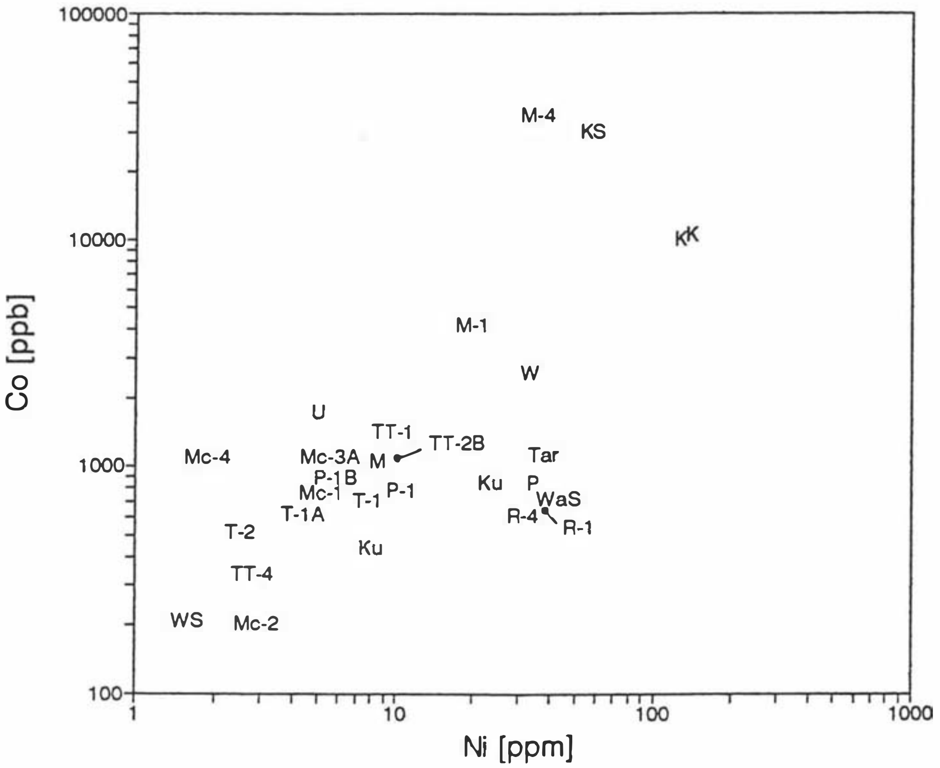


Figure 67: Manganese (ng/g) versus Fe (ng/g) for asphaltenes

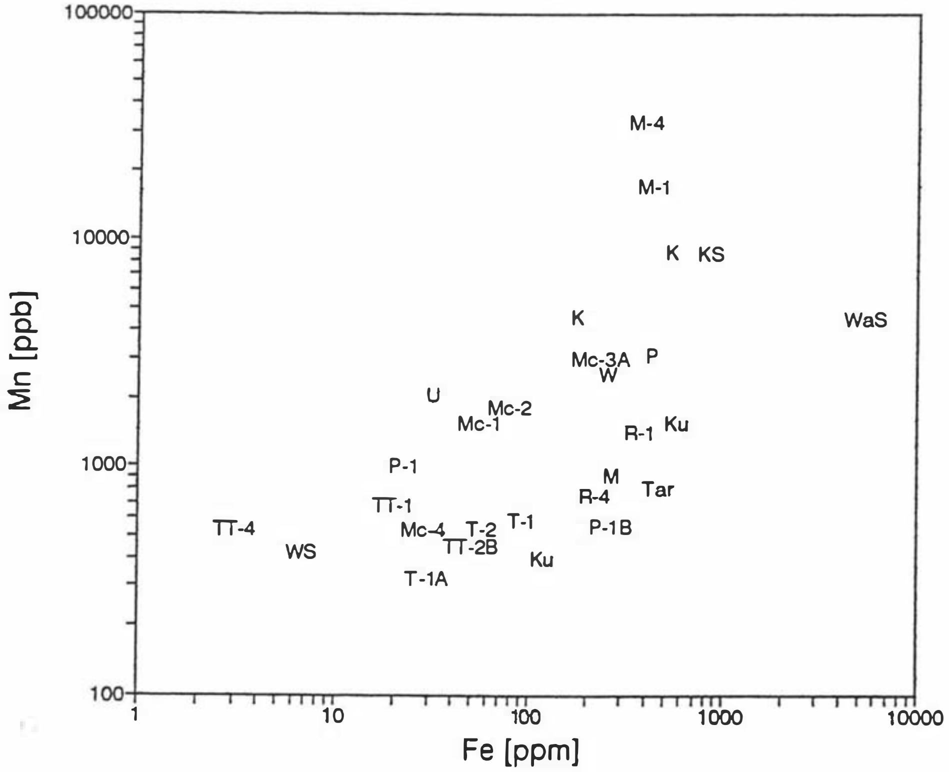


Figure 68: Cobalt (ng/g) in asphaltenes and maltenes

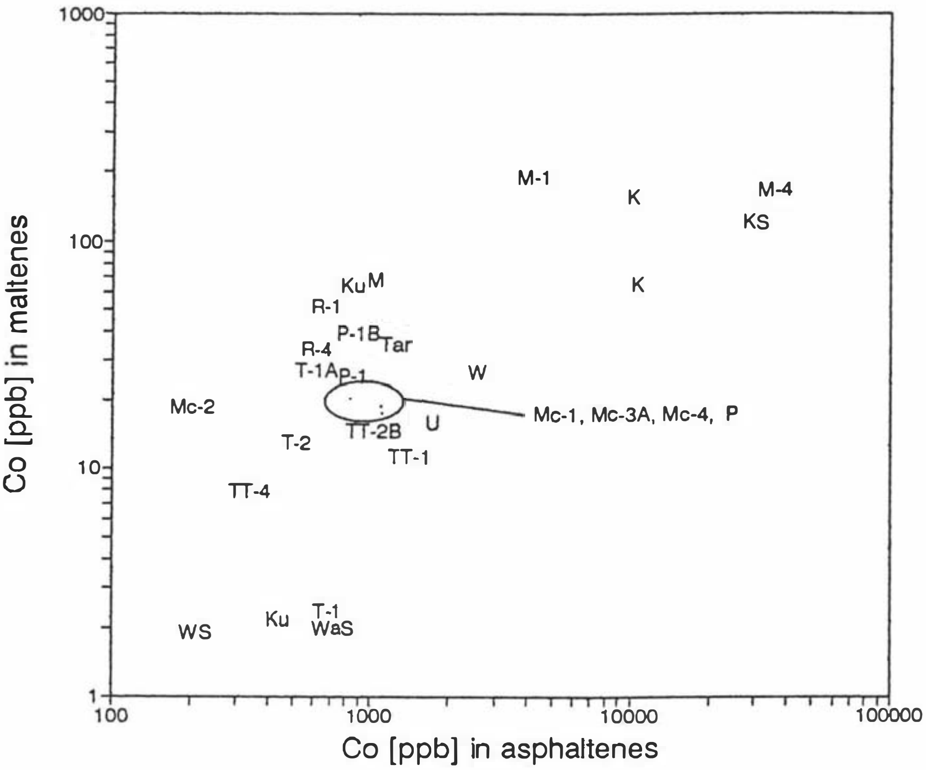


Figure 69: Nickel (µg/g) in asphaltenes and maltenes (NZ oils)

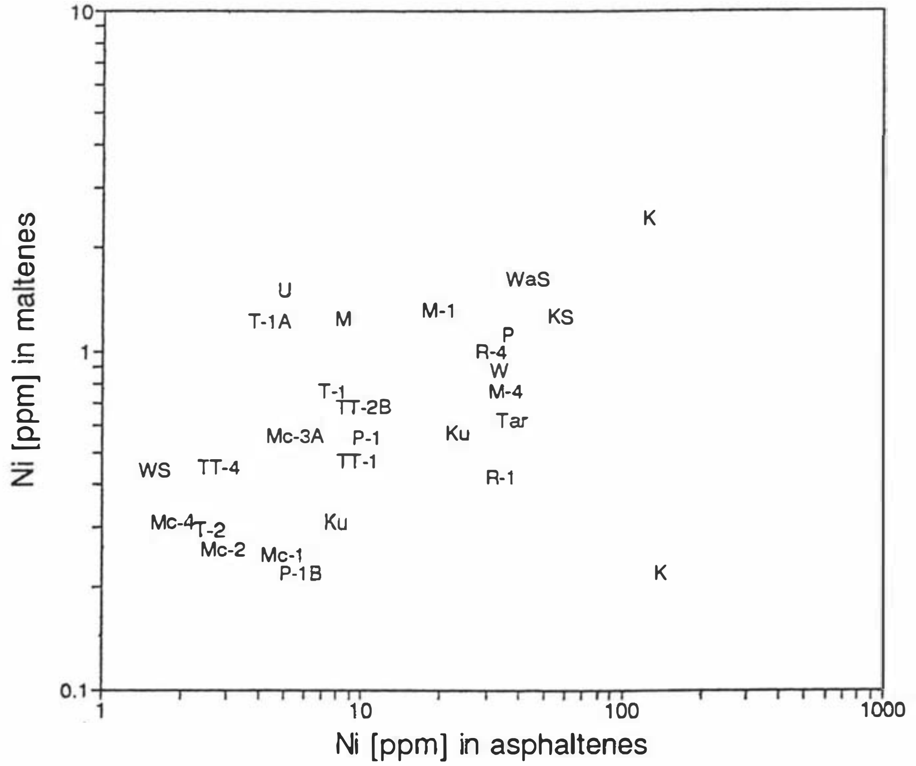
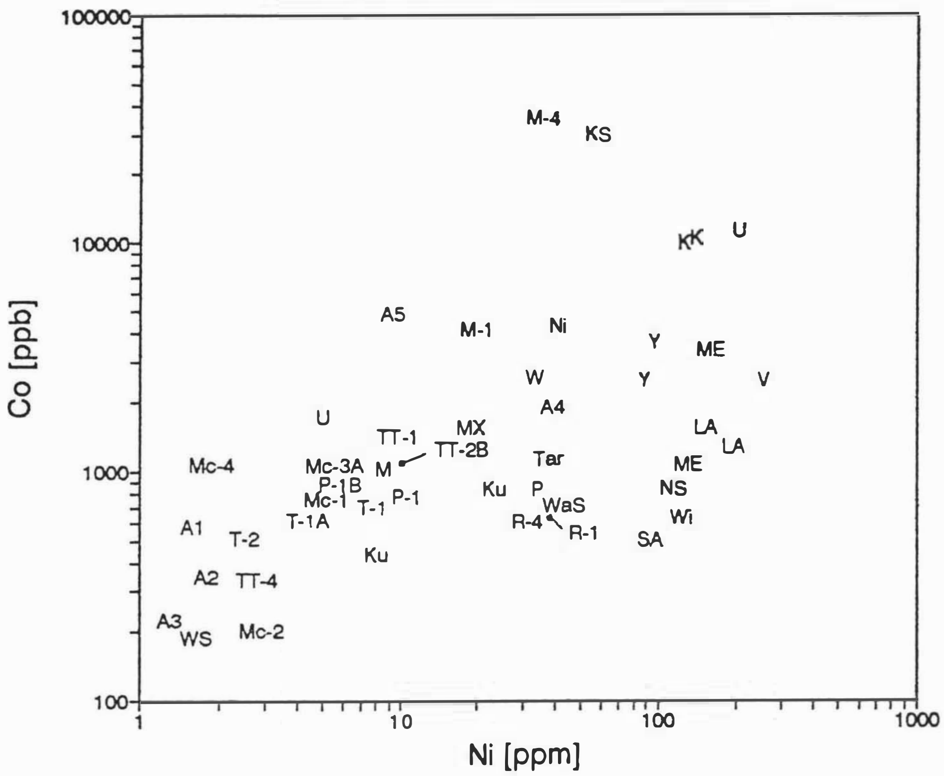


Figure 70: Cobalt (ng/g) versus Ni (µg/g) for New Zealand and some overseas asphaltene samples



K	Kora,DST2	A1	Brumby-2
K	Kora, DST3	A2	Gidgealpa-20 (Namur Sst)
KS	Kotuku Seep	A3	Gidgealpa-20 (Birkhead)
Ku	Kupe-2	A4	Gidgealpa-16
Ku	Kupe-3	A5	Gidgealpa-17
M-1	Maui-1	SA	Saudi-Arabia
M-4	Maui-4	V	Venezuela
Mc-1	McKee-1	Y	Yumen #503
Mc-2	McKee-2	Y	Yumen #506
Mc-3A	McKee-3A	Ni	Nigeria, marine oil
Mc-4	McKee-4	NS	North Sea, # 3168, low mat.
M	Moki-1	MX	Gulf of Mexico, # 41054
P-1	Pouri-1	ME	Middle East, # 4677
P	Pukearuhe-1	U	Uinta Basin, # 19126
P-1B	Pukemai-1B	Wi	Williston Basin, # 22966
R-1	Republic-1	ME	Middle East, #5220, low mat.
R-4	Republic-4	LA	Los Angeles Basin
TT-1	ToeToe-1	LA	Los Angeles Basin
TT-4	ToeToe-4		
Tar	Taranaki-5		
T-1A	Tariki-1A		
TT-2B	ToeToe-2B		
T-1	Toru-1		
T-2	Tuhua-2		
U	Urenui		
W	Waihapa		
WS	Waiotapu Seep		
WaS	Waitangi Seep		

V. CONCLUSIONS

This study has provided information relevant to the determination of trace elements in crude oils, and to the use of trace element concentrations and distributions in terrestrial and marine-derived oils in petroleum geochemistry and geology.

5.1 ANALYTICAL METHODS

Instrumental NAA and GFAAS were successfully used for the determination of trace elements in crude oils. Both methods have their distinct advantages and disadvantages and complement one another in the analysis of crude oils, as a wide range of elements can be determined at low concentrations.

Instrumental NAA allowed the quantification of a wide range of elements, including halogens and rare earth elements, that are usually difficult to determine by other methods. The use of undiluted and untreated oil samples is one of the advantages of INAA, as it minimizes contamination. Some elements, such as Ni, could not be determined at low concentrations with INAA and results obtained with this method, usually showed large errors.

Graphite furnace AAS was used to determine elements that could not be quantified by INAA. The analysis of oil solutions by GFAAS was very difficult, partly due to the low concentrations of elements in New Zealand oils and accurate results could only be obtained if well matched standard matrices were used and the spreading of oil solutions was minimized. A mixed solvent system allowed the determination of elements, such as Cd, Cu, Pb and Zn using aqueous standard solutions. Vanadium could only be determined in aqueous solutions, as organic oil solutions gave inaccurate results due to possible reactions of the element with the graphite and matrix effects.

Ashing of crude oil samples resulted in considerable losses of trace elements, due to volatility. The acid oxidation of the organic matrix required large amounts of reagents, the resulting solutions showed considerable contamination and the technique also gave poor reproducibility. Both techniques were not a viable alternative for the analysis of crude oil samples by GFAAS.

5.2 TRACE ELEMENT DATA

The trace element concentrations in New Zealand oils, especially the low V and Ni values, confirm the terrestrial origin of the Taranaki Basin oils.

A comparison with other oils of terrestrial origin from Australia, China and Nigeria shows that the low Ni and V contents are normal in oils derived from landplant matter, although Chinese oils have a slightly higher Ni content. Nickel and V are useful for the discrimination of oils with low and medium maturity. Furthermore, crude oils can be separated according to their terrestrial, lacustrine and marine origin, solely on their Ni and V content. New Zealand oils with marine influence can only be identified by their slightly higher Ni contents, as all other trace elements concentrations do not show any significant variations compared with other Taranaki oils. Oils from the Taranaki Basin cannot be further subdivided using only their V and Ni values, as the V concentrations vary considerably.

The large variations in trace element concentrations observed in New Zealand oil samples could partly be the result of trace element variations in the original source rock. *Chyi* and *Medlin (1990)* report on the natural variability of elements in coal beds. Trace element differences can be due to regional, local, and in-bed variations. Regional elemental variations are mainly due to sedimentological changes. Local variations within a small area or mine can be caused by the different dispersion of an element as a result of small scale disturbances, such as faults, joints or channel deposits. Other factors contributing to the element abundance in coal beds are the permeability and porosity of overlying rocks, that affect the elemental distribution. Higher or lower concentrations of particular elements, such as Co, K, Fe and Mn, can be found at the top or bottom of a coal seam. These in-bed variations should have little effect on the trace element content of hydrocarbons produced from coal, as migration and accumulation in a reservoir might mix the oil sufficiently to overcome this problem. Local and regional trace element variations of a coal bed could have an influence on the trace element content of hydrocarbons. The element concentrations are also increased or decreased by elements added to, or lost from, surrounding rocks through ground water processes. As not many wells have reached the potential source rocks in the Pakawau group, an exact and comprehensive study and comparison of extracts and coal samples to check for local and regional trace element differences, is not possible. Analysed outcrop samples can only give an indication and although, they belong to the same formation, might result in very different trace element abundances. Extracts from well cuttings and coals could not be linked to their respective oils, although hydrocarbons produced by pyrolysis resemble the Taranaki oils closely. A definite relationship could not be established due to the large variations in element concentrations in oils.

The comparison of trace element contents of New Zealand oils with marine and lacustrine oils from other geographical areas shows, that the Taranaki Basin oils differ from other terrestrial oils in their concentrations of elements associated with clay. Clay elements, such as Al, Cr, Fe, Na and Sc occur in amounts comparable to, or exceeding, the concentrations of these elements in marine and other oils. Other elements occur in low abundances, similarly in New Zealand and terrestrial oils. This fact and the very highly significant correlations of these elements as well as V, occurring only in New Zealand oils, point to the existence of finely dispersed clay minerals in the oils. This would influence certain trace element concentrations considerably, as they are very low and clay would especially affect the very low V content. Vanadium and Ni are commonly used to group oils, but any contribution of clay to the original V concentration would mask any interelemental relationship between oils, as concentrations ranges are extremely low.

Clay could have been accumulated during migration, as kaolinite is present in many Taranaki wells. The contribution of clays to the formation of oils could also mean that part of the minerals originated in the source rock and migrated with the oils. Well water and bitumen samples could not help to shed any more light on the origin of clay minerals. As clay elements are not enriched in the asphaltene fractions, they must be contained in other oil fractions and have very probably been accumulated during migration.

Chinese lacustrine oils contain high concentrations of Ni, as well as Br and Cl. Bromine and Cl were probably incorporated into the oils during migration through salt-rich rock layers or in the reservoirs, as the concentrations of these elements in the Yumen source rock are not higher than in any other extract.

Element concentrations in marine oils of medium and low maturity are generally higher than in terrestrial oils. Trace element contents vary very strongly with maturation level of oils, as high maturity oils are very low in polar components and therefor low in trace elements. As the trace element amounts in New Zealand oils are very low, the slight variations in maturity might be reflected in differences of the trace element concentrations.

Statistical analysis allows for differentiation of marine, lacustrine and terrestrial oils of similar maturity. Oils of the same basin are usually tightly clustered. The wide spreading of New Zealand oils in graphs and element ranges indicates that other factors contribute to the trace element content in New Zealand oils.

The low amounts of asphaltenes confirm the terrestrial origin, although parts of the original asphaltene fraction could have been lost during migration. Trace element concentrations in asphaltenes point to a common or very similar source for the onshore Taranaki oils. Maui-1, Maui-4, Kora-1 and Kotuku Seep oils distinctly differ in their trace element concentrations in asphaltenes from other Taranaki samples.

Trace element analysis of Taranaki Basin and other New Zealand oils confirms their terrestrial origin. The marine influence in oils from the North Taranaki Basin and the Waitangi seep oil is apparent by their slightly higher Ni content. No subdivision of oils into groups could be achieved as the Taranaki oils contain finely dispersed clay affecting their trace element content. Analysis of the polar asphaltene fraction could differentiate between Kora-1, Maui-4, Maui-1 and Kotuku Seep oil and showed that it is likely that the on-shore oils in the Taranaki Basin could have a common or similar source, although the trace element content vary quite considerably.

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APPENDICES

APPENDIX A: Trace elements concentrations in New Zealand oils

Well	Al (ppm)	As (ppb)	Br (ppb)	Cl (ppm)	Co (ppb)	Cr (ppb)	Cs (ppb)	Eu (ppb)	Fe (ppm)	Mn (ppb)	Na (ppm)	Ni (ppm)	Sb (ppb)	Sc (ppb)	Sm (ppb)	V (ppb)	Zn (ppm)
Ahuroa-2	4.38	5.59	1.60	8.42	16.10	254.00	9.90	3.35	7.42	43.40	3.18	0.22	39.70	0.45	0.16	51.7*	0.07
Blackwater	3.55	12.10	100.70	121.00	3.61	61.40	9.48	5.20	3.12	69.50	2.00	0.48	14.70	0.40	0.33*	35.6*	0.28
Galleon-1	3.09	14.28*	71.32	12.20	17.80	283.00	19.30	4.21	29.40	74.90	52.10	0.28	51.00	7.96	3.84	39.4*	0.29
Kaimiro-1	1.94	11.70	39.47	7.41	8.66	182.00	6.38	4.83	7.19	40.80	3.02	0.33	27.40	0.53	0.19*	15.8*	0.30
Kapuni Cond.	58.00	43.10	77.99	15.20	20.50	340.00	9.04	8.79	36.10	313.00	73.30	0.36	30.60	9.15	4.05	465.0	0.32
Kora-1, DST2	3.43*	17.91	81.69	20.17	193.47	70.60	4.27	1.78	14.80	272.48	12.58	2.87	13.85	0.44	0.35*	191.0	11.64
Kora-1, DST3	7.53*	6.78	66.67	8.13	92.52	35.07	5.91	12.29	10.35	971.37	2.16	0.96	16.12	3.01	40.01	301.0	12.68
Kotuku Seep	13.10	9950.00	39.40	7.64	176.00	146.00	8.91	2.58	9.40	543.00	2.83	1.36	12.40	0.42	0.44*	94.5	0.75
Kupe South-1	71.90	45.70	28.12	13.80	25.70	263.00	9.07	5.56	46.00	264.00	68.00	0.60	30.50	9.82	4.55	454.0	0.08
Kupe South-2	2.67	8.32	211.52	19.45	2.87	80.60	9.75	4.35	6.78	44.38	6.42	0.32	20.59	0.39	0.33*	29.5	0.77
Kupe South-3	5.88	54.12	160.80	35.51	68.06	116.24	5.26	3.60	28.60	190.33	30.32	0.68	7.25	0.43	0.35*	74.9	5.40
Kupe South-4	1.32	10.08	37.59	8.96	12.72	19.82	4.35	1.79	4.04	21.51	1.23	0.18	4.51	0.36	0.19*	17.6	0.35
Kupe South-5	6.04	8.49	44.14	9.80	4.20	26.40	5.14	1.21	1.54	26.25	1.79	0.21	7.57	0.52	0.15*	83.0	0.13
Maui-1	159.00	175.00	444.96	56.90	226.00	49.90	18.10	9.87	4.83	151.00	124.00	1.47	115.00	18.10	11.70	320.0	1.33
Maui-3	55.80	11.90	107.45	7.80	17.20	297.00	8.37	4.44	29.30	196.00	54.40	0.16	41.80	8.02	3.74	445.0	0.16
Maui-4	13.60	30.00	204.76	39.20	326.00	372.00	3.96*	5.03	19.80	365.00	60.20	0.91	34.20	1.54	0.94	107.0	0.59
McKee-1	40.70	16.20	111.51	15.60	25.50	355.00	17.20	3.23	32.50	218.00	49.00	0.27	39.60	6.89	3.56	368.0	0.30
McKee-2	29.64*	16.60	829.27	96.00	19.10	55.40	7.88	4.57	5.89	57.10	97.70	0.27	6.80*	0.56	0.48*	27.0	0.19
McKee-3A	53.20	18.10	170.96	11.70	22.80	350.00	7.38*	4.86	32.90	227.00	60.30	0.57	54.30	9.02	4.41	437.0	0.14
McKee-4	55.70	18.80	151.44	9.16	23.50	329.00	14.20	3.93	35.60	257.00	57.60	0.32	53.40	9.56	4.25	445.0	0.33
Moki-1	208.00	29.90	523.02	88.50	69.80	333.00	15.70	5.45	43.40	300.00	130.00	1.26	43.80	11.10	4.12	577.0	1.05
Moturoa	26.90	71.50	1900.70	403.00	42.00	151.00	5.12*	3.86	132.00	625.00	312.00	0.84	21.10	2.01	0.66	123.0	4.18
Pouri-1	62.20	60.20	145.09	13.40	28.00	320.00	14.50	6.82	29.90	291.00	0.83*	0.57	49.30	9.09	4.36	647.0	0.30
Pukearuhe-1	22.00	47.50	158.03	46.30	151.00	394.00	8.40*	2.94	50.60	513.00	10.40	1.68	99.00	3.70	2.63	80.5	3.30
Pukemai-1B	7.80*	15.50	138.00	8.83	44.10	240.00	7.24	1.58	5.98	177.00	3.91	0.25	19.20	0.58	0.28	95.4	2.52
Pukemai-2	2.17	3.74	28.32*	8.75	6.77	50.80	12.40	4.44	3.21	33.40	1.41	0.12	16.40	0.17	0.19*	22.4*	0.29
Republic-1	5.75	19.70	36.51	40.90	54.40	139.00	7.96	2.60	13.70	123.00	33.10	0.56	6.00*	0.64	0.28	145.0	3.30
Republic-4	32.30	36.90	61.51	13.60	36.20	294.00	10.40	4.76	52.60	519.00	16.60	1.23	41.50	3.75	1.71	168.0	1.60
Stratford-1	70.10	17.80	47.51	13.30	15.90	282.00	11.50	6.88	28.60	290.00	60.60	0.27	23.70	9.64	3.71	448.0	0.17
Stratford-1	65.30	21.80	65.04	15.40	18.40	314.00	6.12*	4.13	25.70	193.00	57.80	0.32	20.80	8.10	4.14	460.0	0.34
Taranaki-5	107.00	41.20	158.24	19.60	38.50	259.00	7.86	6.15	61.90	540.00	59.50	0.67	50.40	26.90	9.06	522.0	2.02
Tariki-1	45.40	13.00	72.53	12.30	28.30	761.00	6.63	3.94	29.50	231.00	47.40	1.22	38.40	7.14	3.17	385.0	0.40
Tariki-1A	6.25	3.56*	10.09	12.40	3.14	71.80	26.60	5.03	2.30	40.50	0.64	0.16	7.00*	0.53	0.21*	39.0*	0.05
ToeToe-1	23.40*	11.90	48.01*	11.70	12.40	36.30	8.55	7.82	2.83	33.30	3.61	0.48	26.90	0.26*	0.66	50.0	0.33
ToeToe-2B	19.26*	9.79	14.39	15.00	16.10	45.00	12.40	3.82	4.00	55.70	5.62	0.69	19.70	0.32	0.21*	50.0	0.44
ToeToe-3	8.69	21.50	10.44	7.22	24.80	154.00	9.13	6.85	13.50	121.00	3.86	0.61	48.40	1.21	0.34	35.2	0.43
ToeToe-4	13.50	13.50	45.62	8.87	8.40	70.20	8.33	5.03	7.26	51.50	9.35	0.45	11.90	1.54	0.67	143.0	0.32
Toru-1	2.54	8.77	75.22	23.32	4.43	98.60	4.55	3.19	7.17	97.82	10.47	0.78	19.58	0.60	0.31*	34.6	0.88
Tuhua-1	52.10	67.00	119.87	9.10	22.40	274.00	26.60	8.37	29.50	197.00	51.60	0.34	52.50	7.27	3.38	376.0	0.19
Tuhua-2	13.70	66.70	49.45	8.21	13.40	169.00	6.25	2.16	7.08	80.00	11.30	0.30	14.40	1.64	0.85	108.0	0.59
Tuhua-2, A-Sand	40.68*	22.10	48.04*	13.90	12.70	88.90	14.70	5.65	7.30	68.60	9.94	0.35	9.18*	1.83	0.63	214.8	0.23
Tuhua-2, B-Sand	5.26*	23.30	38.77*	9.57	22.00	41.10	11.70	6.99	2.58	34.40	3.54	0.71	27.60	0.36	0.12*	30.0	0.42
Urenui-1	67.40	15.80	1198.91	77.90	17.90	394.00	9.60*	6.48	35.00	270.00	119.00	1.50	63.20	9.94	4.28	584.0	0.15
Waihapa	6.67	23.05	171.72	32.66	35.95	40.37	2.95	2.18	2.74	20.52	26.11	1.06	13.91	0.21	0.34*	112.5	0.19
Waiotapu Seep	11.90	28100.00	122.42	14.00	7.15	168.00	7.36	4.30	8.89	175.00	6.50	0.47	29.30	0.58	1.10*	113.0	2.14
Waitangi Seep	69.40	109.00	333.00	210.00	12.20	169.00	5.74	4.91	167.00	460.00	6.76	2.20	25.40*	13.20	17.37	463.9	4.59

NB: * values were below the limit of detection
and are shown as 60% of this limit

APPENDIX B: Trace element concentrations in overseas oils

	Al (ppm)	As (ppb)	Br (ppb)	Cl (ppm)	Co (ppb)	Cr (ppb)	Cs (ppb)	Eu (ppb)	Fe (ppm)	Mn (ppb)	Na (ppm)	Ni (ppm)	Sb (ppb)	Sc (ppb)	Sm (ppb)	V (ppb)	Zn (ppm)
Hutouya-1, China	*18.4	3820.0	188.0	525.0	29.8	30.2	2.8	2.0	3.20	21.7	17.60	2.57	21.5	0.2	*0.5	*340.2	0.26
Toucan-1, China	*7.5	390.0	101.0	559.0	291.0	28.0	7.5	3.5	1.48	22.4	3.37	5.33	5.4	0.4	*0.4	482.0	0.30
Taican-1, China	*10.7	71.7	124.0	7.9	7.7	76.4	4.2	2.7	4.11	37.6	5.50	0.23	20.8	0.2	*0.4	*126.0	0.74
Timor Sea	*3.2	11.7	66.4	5.5	8.8	21.4	3.9	2.1	1.63	15.4	1.27	1.01	6.0	0.2	*0.2	326.0	0.38
Nigeria, landplant	*2.9	7.9	41.1	28.7	3.2	30.2	3.1	1.3	6.69	37.2	7.99	0.59	2.9	0.2	*0.3	*59.0	0.32
Merrimelia-6, Namur Sst.	1.4	18.4	49.0							16.8		0.31				*22.6	
Merrimelia-6, Hutton Sst.	*2.0	7.4	90.3							27.3		0.25				*35.3	
Merrimelia-6, Murta M.	7.8	5.6	46.6							32.7		0.29				94.8	
Merrimelia-12	351.0	48.0	959.2							2996.0		1.01				688.9	
Strzelecki-3	*3.8	20.3	48.7							36.5		0.70				*59.8	
Strzelecki-5	2.5	37.1	52.5							34.0		0.63				*23.0	
Strzelecki-10	2.3	49.3	59.3							42.5		0.78				*23.1	
Spencer-5, Birkhead Fm.	4.7	26.6	39.7							58.0		0.40				*28.8	
Spencer-5, Namur Sst.	*3.6	24.0	40.0							50.7		0.40				*46.1	
Taloola-1	11.3	13.0	156.5							184.7		0.65				*138.2	
Tantanna-1	22.8	*215.6	387.7							262.5		0.64				152.4	
Dullingari-29, Murta M.	2.7	18.2	40.1							46.0		0.43				*22.5	
Dullingari-29, Namur Sst.	2.5	9.9	40.0							45.3		0.40				*20.3	
Lepena-1, Patch. Fm.	9.2	13.0	45.6							117.0		0.05				98.8	
Lepena-1	5.9	9.7	45.0							57.1		0.14				65.4	
Wancoocha-2, Murta M.	2.6	27.4	42.9							51.3		1.73				*29.0	
Wancoocha-2, Patch. Fm.	2.6	123.7	68.5							66.3		0.53				*17.5	
Wancoocha-2, Birkhead Fm.	3.5	19.4	53.3							26.6		0.41				*56.7	
Kidman-5	3.5	*2.7	34.3							70.3		0.58				58.2	
Meranji-1, Patchawarra Fm.	4.4	3.9	49.5							72.0		0.31				61.3	
Meranji-1, Namur Sst.	1.5	17.8	42.7							41.7		0.63				*26.6	
Gidgealpa-16	206.1	156.9	6253.0							1373.0		2.63				398.6	
Gidgealpa-17	6.9	23.2	53.2							67.9		0.57				74.6	
Gidgealpa-20, Birkhead Fm.	4.8	11.4	33.4							62.4		0.43				*40.4	
Gidgealpa-20, Namur Sst.	*3.3	28.9	33.2							48.0		0.97				*41.6	
Big Lake-37	2.6	22.2	43.8							65.2		0.21				*25.3	
Alwyn-1	5.1	37.7	89.7							55.5		0.90				47.3	
Bagundi-1	2.4	4.7	39.8							25.8		0.54				264.0	
Brumby-2	8.4	51.6	513.1							156.4		0.79				*45.4	
Florence-7A, USA	2.8	14.6	54.7							71.3		0.43				*23.1	
Florence-8A, USA	4.3	6.8	39.4							49.9		0.55				*64.1	
Mansfield-1A, USA	3.5	20.2	47.1							47.8		0.38				*25.6	
Yumen #114	*18.6	841.0	14600.0	2650.0	1270.0	79.4	103.5	9.2	13.80	191.0	2140.00	44.10	20.5	0.6	*6.5	771.0	5.24
Yumen, #503	*61.2	704.0	485.0	2160.0	1060.0	51.8	6.7	1.0	6.17	97.8	5.26	36.20	28.6	*0.20	*0.5	874.0	23.70
Yumen, #502	*18.3	671.0	338.0	1350.0	1040.0	54.1	3.9	2.6	5.75	32.8	6.80	35.30	18.8	*0.20	*0.5	766.0	1.66
Yumen, #508	*4.5	467.0	500.0	731.0	557.0	40.1	5.9	2.9	5.94	36.4	41.80	19.50	185.0	0.1	*0.7	643.0	2.97
Yumen, #507	*21.1	639.0	2170.0	2970.0	976.0	76.3	6.3	2.7	9.11	56.6	564.00	34.10	25.5	*0.21	*1.9	569.0	2.16
Yumen, #194	*73.8	913.0	469.0	5060.0	819.0	212.0	3.7	1.8	13.60	106.0	17.80	22.00	17.8	0.6	*0.4	*1218.0	2.32
Yumen, #88	*5.1	547.0	301.0	1670.0	620.0	96.0	3.5	0.8	6.87	87.1	72.80	19.30	24.0	0.3	*0.6	814.0	1.99
Prudhoe Bay	*46.9	115.0	275.0	2570.0	39.4	51.2	5.2	1.6	1.58	35.5	32.00	16.50	12.3	0.3	0.5	31100.0	2.55
Saudi-Arabia	4.4	33.4	180.2	12.9	5.6	50.2	5.0	3.1	3.53	21.8	3.60	4.15	13.9	0.4	*0.4	16315.0	0.72
OMC 4755, N.S.	*6.4	3.1	46.1	25.7	2.7	20.5	8.1	3.0	1.84	30.3	1.89	0.64	4.3	0.5	*0.2	15600.0	0.13
OMC 3168 N. Sea	18.2	172.2	1960.0	811.4	25.7	447.1	6.1	1.6	29.43	416.0	185.23	4.43	29.8	2.0	1.7	34100.0	7.80
OMC 5217 N. Sea	1.8	3.2	169.6	13.9	*2.51	82.3	2.5	1.0	1.94	18.0	0.97	0.30	12.7	0.5	0.4	*17.32	0.34
OMC 78 Nigeria	*6.4	19.1	68.5	9.3	30.6	25.0	5.8	2.7	7.89	413.8	5.03	1.16	7.3	0.6	*0.2	654.2	0.46
OMC 4677 M. East	13.3	74.6	139.1	52.2	51.0	2642.0	1042.0	3.4	61.74	708.6	21.26	3.27	2.0	3.3	*0.5	201.7	21.45
OMC 5220 M. East	*25.8	2507.0	4198.0	717.4	128.4	1253.0	4.1	3.6	93.12	354.6	15.77	6.95	465.7	57.8	0.7	5266.0	31.96
OMC 5363 M.E	*33.3	5.0	49.3	24.4	2.8	77.4	3.0	1.8	9.73	43.4	2.27	0.17	9.6	0.2	*0.2	264.7	0.21
Venezuela	*11.9	203.0	89.7	17.2	897.0	305.0	*4.5	4.7	18.90	746.0	17.40	55.40	33.5	7.3	5.1	367000.0	1.18
Quiketal Seep	29.4	201.7	85.4	52.1	29.2	6240.0	12.6	28.8	47.70	1883.0	50.33	1.79	24.7	1100.0	97.0	2709.0	67.19
Yumen oilsand	241.4	764.9	17924.0	250.8	832.6	619.0	28.8	10.8	92.76	570.2	35.45	27.87	60.9	39.5	34.2	2322.0	11.08
Minghe B. oilsand	63.5	575.2	1863.0	156.7	43.0	545.3	40.8	38.5	17.93	392.1	10.18	2.46	122.8	62.8	78.3	302.4	11.31
Dorset oilsand	929.3	2222.0	27930.0	228.3	2495.0	1414.0	47.9	98.7	999.25	39139.0	121.80	10.70	137.9	558.0	360.4	*2670.6	18.00

* values were below the limit of detection and

APPENDIX C: Trace element concentrations in overseas oils

	Al (ppm)	Co (ppb)	Fe (ppm)	Mn (ppb)	Ni (ppm)	V (ppm)
154627 A (Hondo-3, Los Angeles)	3.57	109.3	1.93	63.7	58.34	23.20
154627 B (Hondo-5)	4.46	120.1	2.06	69.9	55.93	21.00
154627 D (Hondo-9)	5.76	124.3	3.51	75.9	55.13	21.00
154627 E (Hondo-12)	4.13	173.8	7.63	83.2	38.20	20.89
154627 F (Hondo-22)	3.70	117.7	2.53	186.9	57.33	21.00
154627 H (Hondo-24)	4.20	103.2	3.28	197.6	47.33	23.00
154627 K (Hondo-37)	0.86	111.7	3.09	62.7	50.33	25.00
19125 (Alfreda Knudsen-1, Uinta)	36.64	346.1	32.89	390.5	13.09	9.94
21850 (Orlan Johnson-1, Uinta)	6.22	262.2	10.29	52.1	7.85	0.75
22966 (Texas-1B, Williston)	4.36	80.1	3.05	60.0	23.80	79.47
22970 (R.P. Oliver-4, Will.)	2.82	135.2	1.13	23.4	15.01	14.65
22971 (Continental-1, Will.)	1.91	107.6	3.64	11.0	14.95	8.32
22974 (McAlister Fuel, Will.)	0.47	189.6	3.53	10.1	23.97	42.54
41054 (Humble-3, G. of Mexico)	1.89	157.1	0.62	14.8	5.00	1.20
41056 (Clark Oil Co. G. of Mex.)	0.92	185.7	8.38	88.1	5.81	10.05
48101 (Husky M. Rainbow, Alberta)	2.44	37.5	5.62	47.6	1.03	0.75
51577 (Imperial-Legal, Alb.)	2.06	38.8	7.88	15.8	0.44	4.45
54051 A (25/11-1, North Sea)	1.62	417.8	2.50	584.5	1.58	9.41
56323 (25/8-1, North Sea)	0.89	340.0	2.92	95.5	7.32	16.52

APPENDIX D: Nickel/V and V/Ni ratios for New Zealand oils

	Ni/V	V/Ni
Ahuroa-2	4.26	0.24
Blackwater	13.48	0.07
Galleon-1	7.11	0.14
Kaimiro-1	20.89	0.05
Kapuni Cond.	0.77	1.29
Kora-1, DST2	15.03	0.07
Kora-1, DST3	3.19	0.31
Kotuku Seep	14.39	0.07
Kupe South-1	1.32	0.76
Kupe South-2	10.85	0.09
Kupe South-3	9.08	0.11
Kupe South-4	10.23	0.10
Kupe South-5	2.53	0.40
Maui-1	4.59	0.22
Maui-3	0.36	2.78
Maui-4	8.50	0.12
McKee-1	0.73	1.36
McKee-2	10.00	0.10
McKee-3A	1.30	0.77
McKee-4	0.72	1.39
Moki-1	2.18	0.46
Moturoa	6.83	0.15
Pouri-1	0.88	1.14
Pukearuhe-1	20.87	0.05
Pukemai-1B	2.62	0.38
Pukemai-2	5.36	0.19
Republic-1	4.24	0.24
Republic-4	7.32	0.14
Stratford-1	0.60	1.66
Stratford-1	0.70	1.44
Taranaki-5	1.28	0.78
Tariki-1	3.17	0.32
Tariki-1A	4.10	0.24
ToeToe-1	9.60	0.10
ToeToe-2B	13.80	0.07
ToeToe-3	17.33	0.06
ToeToe-4	3.15	0.32
Toru-1	22.54	0.04
Tuhua-1	0.90	1.11
Tuhua-2	2.78	0.36
Tuhua-2, A-S	1.63	0.61
Tuhua-2, B-S	23.67	0.04
Urenui-1	2.17	0.46
Waihapa	9.42	0.11
Waiotapu S	4.16	0.24
Waitangi S	4.74	0.21

APPENDIX E: Trace element concentrations determined with mixed-solvent system

	Cd (ppb)	Cu (ppm)	Pb (ppm)
Ahuroa-2	28.0	0.04	<0.02
Blackwater	39.1	0.05	<0.02
Galleon-1	21.1	0.02	0.18
Kaimiro-1	29.8	0.07	0.07
Kapuni Cond.	63.5	0.14	0.67
Kora-1 DST2	225.8	1.57	1.51
Kora-1 DST3	644.3	1.10	0.70
Kupe South	<5.0	0.18	0.11
Kupe-2	61.3	0.82	0.18
Kupe-3	231.8	0.36	0.61
Kupe-4	38.2	0.13	0.10
Kupe-5	27.0	0.17	0.08
Maui-3	13.3	0.03	<0.02
Maui-4	182.7	0.14	0.74
McKee Cond.	118.9	0.13	<0.02
McKee-2	116.4	0.04	0.28
McKee-3A	117.4	0.23	0.53
Moturoa	164.6	0.69	0.21
Pouri-1	64.4	0.05	0.28
Pukemai-1B	215.8	0.08	1.47
Pukemai-2	9.1	0.02	<0.02
Republic-1	170.1	0.42	0.34
Republic-4	167.7	4.60	1.16
Stratford-1	52.3	0.15	0.05
Stratford-1	36.2	0.09	0.06
Taranaki-5	1050.2	0.40	0.50
Tariki-1	78.5	0.06	0.05
Tariki-1A	28.5	0.10	0.11
ToeToe-2B	79.7	0.05	0.30
ToeToe-3	97.6	0.14	0.22
ToeToe-4	88.7	0.03	<0.02
Toru-1	65.4	1.23	0.45
Tuhua-2	98.8	0.13	0.09
Tuhua-2, A-Sand	48.8	0.08	0.10
Tuhua-2, B-Sand	77.3	0.06	0.14
Merrimelia-6, Hutton Sst.	n.d.	1.06	1.60
Merrimelia-6, Murta M.	n.d.	0.17	0.50
Strzelecki-3	80.6	0.17	1.09
Strzelecki-5	65.9	0.14	0.23
Strzelecki-10	118.1	0.29	0.30
Dullingari-29, Murta M.	<5.0	0.05	0.22
Gidgealpa-17	<5.0	0.19	0.43
Gidgealpa-20, Birkhead Fm.	<5.0	0.04	<0.02
Gidgealpa-20, Namur Sst.	<5.0	0.05	1.38
Alwyn-1	30.6	0.08	0.10
Brumby-2	110.2	0.19	1.60
OMC 3168 N. Sea, low mat.	<5.0	3.51	0.59
OMC 5217 N. Sea, high mat.	<5.0	0.31	1.14
OMC 78 Nigeria, marine	<5.0	1.26	0.37
OMC 4677 Middle East, med. mat.	<5.0	5.02	1.68
OMC 5220 M. East, low mat.	<5.0	3.87	0.69
OMC 5363 M.East, high mat.	<5.0	1.77	0.25
154627 A (Hondo-3, Los Angeles)	15.9	0.07	0.28
154627 B (Hondo-5)	20.6	0.65	0.31
154627 E (Hondo-12)	32.9	0.92	0.22
154627 F (Hondo-22)	30.5	1.05	0.20
21850 (Orlan Johnson-1, Uinta)	15.0	1.32	0.50
22966 (Texas-1B, Williston)	24.0	1.14	0.21
22970 (R.P. Oliver-4, Will.)	26.5	0.18	0.06
22971 (Continental-1, Will.)	14.4	0.80	0.51
22974 (McAlister Fuel, Will.)	17.4	0.28	0.62
41054 (Humble-3, G. of Mexico)	53.7	5.97	2.55
41056 (Clark Oil Co. G. of Mex.)	26.0	1.42	0.09
48101 (Husky M. Rainbow, Alberta)	26.6	1.29	0.29
51577 (Imperial-Legal, Alb.)	20.9	0.60	0.25
54051 A (25/11-1, North Sea)	142.7	0.29	6.03

APPENDIX F: Trace element concentrations in bitumen

	Al (ppm)	As (ppb)	Br (ppm)	Cl (ppm)	Co (ppb)	Cr (ppb)	Cs (ppb)	Eu (ppb)	Fe (ppm)	Mn (ppb)	Na (ppm)	Ni (ppm)	Sb (ppb)
Yumen rock	11920.00	1747.0	38.7	6898.96	19697.0	22027.0	3417.0	217.5	4652.68	134890.0	6153.52	166.38	325.6
Waipawa Shale	3356.03	18555.0	84.5	12180.00	3674.0	56424.0	98.2	30.1	2792.96	32646.0	9949.86	96.32	207.3
Waipawa Shale O.Str.	1744.17	33932.0	86.0	1625.95	1978.0	20236.0	182.6	20.8	2279.00	16961.0	4396.62	63.11	234.6
Pritchard Bitumen	1889.11	16950.0	21.0	7119.45	535.7	2898.0	29.5	19.0	305.79	2149.0	2937.94	3.57	249.9
Pritchard B./carb.shale	315.70	12120.0	20.1	6050.35	681.2	3170.0	43.5	36.2	278.11	1668.0	2512.27	7.43	228.4
Mangaraukau coal	909.02	1259.0	13.0	12150.00	1170.0	2636.0	33.5	185.9	153.78	946.6	651.60	15.37	83.6
Wairoa coal	74.62	1410.0	20.7	5577.52	1522.0	2004.0	39.2	14.0	50.03	888.8	2116.13	7.78	150.3
Puponga coal	591.65	872.2	4.1	2571.78	1227.0	4617.0	205.6	101.8	107.23	1847.0	148.77	13.53	43.5
North Cape coal	524.85	1432.0	16.2	19840.00	609.5	5284.0	93.4	16.0	308.24	3693.0	1200.95	17.26	128.5
Maui-4 coal	417.27	513.0	20.4	6819.71	5352.0	3829.0	70.4	240.3	1187.88	1390.0	681.52	13.02	207.8
Toko-1,sample A	109.12	15075.0	7374.2	2294.44	619.7	3364.0	44.5	44.4	39.47	512.8	2100.85	29.41	61.8
Toko-1,sample B	96.29	12205.2	5767.1	2336.86	705.7	1328.0	48.9	79.5	59.70	994.8	628.77	15.33	91.8
Toko-1,sample C	502.70	13162.2	5998.3	5842.44	828.7	4442.0	71.8	39.3	189.44	1636.0	1951.16	16.51	55.3
Kapuni #2 coal sample	2251.18	1377.0	24.8	40970.00	2128.0	14290.0	204.5	50.0	1168.76	14863.0	11450.00	42.51	445.21
Kapuni #4 mudstone	500.34	2027.0	30.6	27630.00	1584.0	7019.0	24.0	27.2	282.05	4591.0	5767.80	62.42	122.52
Wairoa Bit. before pyro.	45.83	679.4	17.5	2374.31	865.5	527.3	29.6	21.5	43.70	493.8	1387.41	2.37	198.7
Mangarakau Bit. before pyro.	201.40	437.3	10.7	2433.62	908.1	2184.0	39.3	28.8	159.30	15625.0	83.44	7.96	87.3
Puponga Bit. before pyro.	1367.03	508.6	8.1	466.91	1086.0	1451.0	39.5	33.4	102.54	964.5	108.20	4.32	245.9
North Cape Bit. before pyro.	55.50	517.9	14.0	566.22	170.9	1969.0	42.7	22.1	60.23	395.2	137.81	2.54	145.9
North Cape Bit. after pyro.	196.87	4114.0	21.9	650.58	178.6	2221.0	33.1	11.5	37.09	1428.0	204.62	2.47	34.7
Wairoa Bit. after pyro	93.30	8268.0	29.2	781.61	1879.0	1053.0	84.0	26.1	148.51	1131.0	238.42	4.53	212.1
Mangarakau Bit. after pyro.	60.33	2237.0	17.3	528.35	1165.0	961.3	55.2	36.6	80.11	635.5	127.98	9.52	41.9
Puponga Bit. after pyro.	77.09	3019.0	20.1	5907.73	2095.0	2619.0	73.8	37.8	130.39	636.6	168.68	13.61	63.6

	Sc (ppb)	Sm (ppb)	V (ppb)	Zn (ppm)
Yumen rock	2104.0	888.1	27050.0	104.25
Waipawa Shale	158.1	697.7	8720.0	1072.28
Waipawa Shale O.Str.	198.9	608.6	4129.0	273.82
Pritchard Bitumen	15.4	15.9	12710.0	147.12
Pritchard B./carb.shale	15.3	7.4	9420.0	122.21
Mangaraukau coal	38.8	8.6	8690.0	28.57
Wairoa coal	42.4	12.0	1350.0	15.59
Puponga coal	111.2	42.7	2160.0	11.26
North Cape coal	44.9	12.8	6230.0	75.55
Maui-4 coal	20.1	11.0	6860.0	54.13
Toko-1,sample A	9.9	460.6	1590.0	47.64
Toko-1,sample B	29.5	260.5	7460.0	45.65
Toko-1,sample C	163.6	205.5	3530.0	66.86
Kapuni #2 coal sample	384.2	71.2	6772.2	21.30
Kapuni #4 mudstone	438.8	29.4	27052.0	23.53
Wairoa Bit. before pyro.	65.3	6.8	1040.0	6.47
Mangarakau Bit. before pyro.	16.5	3.4	2550.0	13.14
Puponga Bit. before pyro.	127.4	21.5	6150.0	4.57
North Cape Bit. before pyro.	11.8	5.0	345.0	3.65
North Cape Bit. after pyro.	6.7	10.8	399.0	10.77
Wairoa Bit. after pyro	70.5	15.2	850.0	25.21
Mangarakau Bit. after pyro.	13.3	4.4	560.0	11.79
Puponga Bit. after pyro.	46.6	14.9	520.0	10.27

APPENDIX G: Trace element concentrations in coal (determined by ICP-ES and GFAAS)

SAMPLE	Al (ppm)	As (ppm)	B (ppm)	Ca (ppm)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (ppm)	K (ppm)	Mg (ppm)	Mn (ppm)	Mo (ppm)
Wairoa	9324.79	3.54	128.13	630.82	0.39	8.35	48.15	20.64	2983.15	4706.71	1954.37	10.51	0.00
Mangarakau	6888.01	0.00	155.96	1949.17	0.12	4.02	12.83	8.75	2050.65	863.25	535.99	9.16	0.64
Puponga	7441.83	1.64	209.27	709.65	0.43	8.12	43.17	15.54	1783.62	2037.52	430.80	11.83	0.00
North Cape	1861.32	2.58	98.78	709.77	0.08	1.88	12.33	7.29	1106.14	280.35	195.94	0.87	0.25
Maui-4	19772.79	4.18	120.49	4926.80	0.00	25.65	19.68	17.89	12126.12	5129.89	2114.47	115.42	0.00
Cook-1	18480.71	10.24	146.55	1594.84	0.81	10.78	40.41	26.40	7478.49	4660.86	1452.06	34.21	2.13
Toko A	14102.51	5.76	96.10	1484.30	0.00	13.00	65.82	11.85	6345.31	3834.34	1281.90	62.04	1.65
Toko B	6909.58	4.26	103.48	853.34	0.34	7.06	34.72	9.63	4116.63	4669.96	682.00	36.62	1.01
Pritchard bitumen	37299.14	12.66	214.30	5343.95	0.00	13.11	14.47	45.21	15534.53	8590.56	3612.36	37.07	0.00
Pritchard bit/carb. shale	6828.69	138.93	574.56	86700.75	0.00	9.42	0.00	16.48	109400.24	3087.04	18107.79	65.93	21.19

SAMPLE	Na (ppm)	Ni (ppm)	P (ppm)	Pb (ppm)	S (ppm)	Se (ppm)	Si (ppm)	Sn (ppm)	Sr (ppm)	V (ppm)	Zn (ppm)
Wairoa	3016.55	15.03	63.28	15.72	263.34	3.34	4206.47	1.47	12.58	34.69	18.08
Mangarakau	1113.98	14.76	922.33	3.21	1678.55	0.00	2456.00	0.35	0.00	44.18	11.90
Puponga	1459.01	8.89	36.60	8.63	1666.87	5.61	2936.15	1.30	12.78	92.03	8.98
North Cape	423.28	8.21	39.64	3.08	660.99	0.00	832.83	0.25	81.80	51.13	6.28
Maui-4	5696.23	18.49	675.20	0.00	1992.19	0.00	9039.42	0.00	136.59	43.57	28.93
Cook-1	3556.05	20.47	1862.62	26.94	1799.58	19.67	8254.36	8.35	155.71	20.74	26.94
Toko A	3982.27	55.95	143.82	14.15	1527.09	0.00	6962.39	2.47	47.39	49.44	18.10
Toko B	2878.06	16.80	51.96	20.16	2035.92	8.29	4517.55	1.79	12.09	21.24	24.64
Pritchard bitumen	13427.69	10.40	268.55	0.00	2161.09	0.00	20996.03	0.00	103.08	71.89	76.86
Pritchard bit/carb. shale	16247.56	9.42	70.64	84.77	34096.33	0.00	43891.96	0.00	348.50	482.13	47.09

APPENDIX H: Trace element concentrations in asphaltenes

ASPHALTENE SAMPLE	Co (ppb)	Fe (ppm)	Mn (ppb)	Ni (ppm)
Kora, DST2	10149.0	532.4	8920.0	124.9
Kora, DST3	10523.8	175.0	4608.0	137.8
Kotuku Seep	30308.0	853.2	8683.6	57.2
Kupe-2	439.2	120.0	396.8	8.0
Kupe-3	855.9	579.9	1569.0	23.5
Maui-1	4226.0	435.8	17290.0	19.8
Maui-4	35946.0	388.8	33190.0	35.3
McKee-1	820.4	55.4	1560.0	5.0
McKee-2	202.8	78.9	1686.2	2.9
McKee-3A	1076.0	234.9	3037.0	5.5
McKee-4	1080.0	28.6	535.9	1.9
Moki-1	1038.0	261.8	850.3	8.5
Pouri-1	783.0	22.6	1002.1	10.5
Pukearuhe-1	849.6	429.5	3129.9	34.0
Pukemai-1B	896.1	269.1	552.9	5.8
Republic-1	674.1	376.4	1427.6	34.1
Republic-4	616.8	220.0	756.0	31.3
ToeToe-1	1425.0	20.2	678.0	9.7
ToeToe-4	338.3	3.1	532.7	2.8
Taranaki-5	1149.5	467.4	810.0	37.4
Tariki-1A	618.8	30.1	324.7	4.4
ToeToe-2B	1031.3	46.6	509.5	10.2
Toru-1	702.7	93.6	586.3	7.8
Tuhua-2	515.9	57.9	538.4	2.5
Urenui	1739.1	31.6	2064.6	5.0
Waihapa	2570.0	244.2	2898.4	33.3
Waiotapu Seep	210.0	6.8	423.0	1.6
Waitangi Seep	723.3	5456.4	4508.9	43.0
Brumby-2	581.6	88.8	13868.2	1.6
Gidgealpa-20 (Namur Sst)	350.0	10.9	936.6	1.8
Gidgealpa-20 (Birkhead)	225.0	30.8	1059.8	1.3
Gidgealpa-16	1917.5	394.0	12568.3	39.0
Gidgealpa-17	4875.5	103.6	2458.0	9.3
Saudi-Arabia	511.8	29.0	590.0	92.8
Venezuela	2509.6	47.0	1560.0	253.8
Yumen #503	2512.2	19.9	1885.5	88.0
Yumen #506	3683.3	28.8	3490.4	96.5
Nigeria, marine oil	4364.7	241.9	2353.2	40.7
North Sea, # 3168, low mat.	846.1	203.4	800.5	113.6
Gulf of Mexico, # 41054	1553.3	76.9	1068.8	18.8
Middle East, # 4677	1088.9	1070.2	1221.2	129.9
Uinta Basin, # 19126	11292.5	227.9	8187.3	203.6
Williston Basin, # 22966	632.0	101.1	199.2	123.5
Middle East, #5220, low mat.	3421.5	1049.0	2467.0	158.6
Los Angeles Basin	1583.0	36.5	3382.0	181.7
Los Angeles Basin	1553.0	90.2	2897.0	151.1

APPENDIX I: Trace element concentrations in kerogen

	Al	As	Cd	Co	Cr	Cu	Fe	Mn	Na	Ni	Pb	S	Si	Sr	Zn
Puponga coal	2191	2.7	0.4	5.2	23.3	6.7	1536	8.6	250	4.6	9.5	1751	358	99.2	3.1
Wairoa coal	3903	2.5	<0.02	2.9	15.8	6.5	1372	0.9	1066	4.6	10.2	1733	231	59.3	6.8
Mangarakau coal	728	3.1	0.47	1.9	3.5	28.2	1105	0.2	102	4.7	8.6	830	195	130.1	3.6
North Cape coal	647	<1.0	<0.1	1.86	1.46	8.9	1738	1.2	109	7.1	<1.0	1749	312	368.5	6.3

all concentrations in ppm

APPENDIX J: Trace elements in formation water

WELL	Al (ppm)	As (ppm)	B (ppm)	Ca (ppm)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (ppm)	K (ppm)	Mg (ppm)	Mn (ppm)	Mo (ppm)	Na (ppm)	Ni (ppm)	S (ppm)	Si (ppm)	Sr (ppm)	Zn (ppm)
Tuhua-1	<0.50	<0.5	34.0	165.0	<0.05	<0.05	<0.05	0.11	0.15	34937	10.0	0.05	0.46	3306.0	0.24	768.0	<2.5	5.80	0.15
Pukemai-2B	<0.50	<0.5	0.2	5.7	<0.05	<0.05	<0.05	<0.05	<0.10	140	<0.8	0.17	<0.05	40.5	<0.1	2.3	<2.5	0.73	0.15
McKee-1	<0.50	<0.5	27.0	10.2	<0.05	<0.05	0.10	2.20	2.60	80	16.5	<0.01	<0.05	4133.0	<0.1	233.0	25.0	5.10	0.16
Pukearuhe	<0.50	<0.5	0.4	71.0	<0.05	<0.05	<0.05	<0.05	3.30	1040	1.3	0.43	0.09	222.0	<0.1	59.0	2.5	2.90	0.62
Kupe South-4	<0.50	<0.5	15.4	261.0	<0.05	<0.05	<0.05	<0.05	42.00	17110	126.0	<0.01	0.10	13992.0	<0.1	1102.0	21.5	14.30	0.13
Kaimiro-1	<0.50	<0.5	8.3	279.0	<0.05	<0.05	<0.05	<0.05	0.36	3283	12.5	<0.01	<0.05	3458.0	<0.1	21.0	3.5	23.50	0.12
Kupe South-1	<0.10	<0.1	73.0	410.0	<0.01	<0.01	<0.01	<0.01	0.12	84	19.7	0.02	<0.01	4831.0	<0.02	6.0	14.3		0.07

APPENDIX K: Correlation matrix for New Zealand oils

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      46 Observations
      16 Variables


                                   Simple Statistics

                      LAL                 LAS                 LBR                 LCL

 Mean         1.222986301         1.433354557         1.988012775         1.275379598
 Std          0.570148111         0.703176052         0.700586917         0.414945393


                      LCO                 LCR                 LCS                 LEU

 Mean         1.358943616         2.197058075        0.9406148899        0.6361216905
 Std          0.483459724         0.454678118        0.2109278401        0.2119155931


                      LFE                 LMN                 LNA                 LNI

 Mean         1.166270226         2.164466944         1.156600940        -.2801836594
 Std          0.510097693         0.479858553         0.687914741        0.3254990842


                      LSB                 LSC                  LV                 LZN

 Mean         1.377980342        0.2644462624         2.111780396        -.2652206662
 Std          0.327012128        0.6427734229         0.488297477        0.5741797773


                                   Correlation Matrix

              LAL       LAS       LBR       LCL       LCO       LCR       LCS       LEU

 LAL       1.0000    0.2564    0.2788    0.2489    0.3037    0.6254    0.3161    0.4477
 LAS       0.2564    1.0000    0.1532    0.1082    0.3090    0.2788    -.0335    0.0141
 LBR       0.2788    0.1532    1.0000    0.4698    0.2658    0.2609    -.1467    -.0939
 LCL       0.2489    0.1082    0.4698    1.0000    0.1827    0.1431    -.1729    0.0604
 LCO       0.3037    0.3090    0.2658    0.1827    1.0000    0.4244    -.1500    0.0306
 LCR       0.6254    0.2788    0.2609    0.1431    0.4244    1.0000    0.3214    0.2960
 LCS       0.3161    -.0335    -.1467    -.1729    -.1500    0.3214    1.0000    0.4605
 LEU       0.4477    0.0141    -.0939    0.0604    0.0306    0.2960    0.4605    1.0000
 LFE       0.6842    0.2888    0.3230    0.4098    0.4866    0.7660    0.1239    0.3289
 LMN       0.6277    0.4323    0.3696    0.3107    0.6684    0.6974    0.0754    0.3509
 LNA       0.6169    0.1152    0.3838    0.4284    0.3850    0.5754    0.0058    0.1868
 LNI       0.2719    0.3497    0.2155    0.4773    0.6067    0.2524    -.2754    0.1144
 LSB       0.5302    0.1481    0.1479    0.0240    0.2880    0.7421    0.3478    0.4543
 LSC       0.8107    0.1102    0.2224    0.1398    0.2611    0.7313    0.3166    0.4460
 LV        0.8382    0.2144    0.2561    0.1185    0.3523    0.5701    0.1392    0.2953
 LZN       -.0689    0.3045    0.3713    0.3361    0.5100    0.0227    -.3627    -.0910

              LFE       LMN       LNA       LNI       LSB       LSC        LV       LZN

 LAL       0.6842    0.6277    0.6169    0.2719    0.5302    0.8107    0.8382    -.0689
 LAS       0.2888    0.4323    0.1152    0.3497    0.1481    0.1102    0.2144    0.3045
 LBR       0.3230    0.3696    0.3838    0.2155    0.1479    0.2224    0.2561    0.3713
 LCL       0.4098    0.3107    0.4284    0.4773    0.0240    0.1398    0.1185    0.3361
 LCO       0.4866    0.6684    0.3850    0.6067    0.2880    0.2611    0.3523    0.5100
 LCR       0.7660    0.6974    0.5754    0.2524    0.7421    0.7313    0.5701    0.0227
 LCS       0.1239    0.0754    0.0058    -.2754    0.3478    0.3166    0.1392    -.3627
 LEU       0.3289    0.3509    0.1868    0.1144    0.4543    0.4460    0.2953    -.0910
 LFE       1.0000    0.8358    0.6791    0.4512    0.6144    0.8310    0.6856    0.3322
 LMN       0.8358    1.0000    0.4885    0.5689    0.5289    0.6934    0.6794    0.5136
 LNA       0.6791    0.4885    1.0000    0.2485    0.3820    0.6041    0.5471    0.0574
 LNI       0.4512    0.5689    0.2485    1.0000    0.3026    0.2090    0.3183    0.5776
 LSB       0.6144    0.5289    0.3820    0.3026    1.0000    0.6492    0.4400    -.0290
 LSC       0.8310    0.6934    0.6041    0.2090    0.6492    1.0000    0.8257    -.0098
 LV        0.6856    0.6794    0.5471    0.3183    0.4400    0.8257    1.0000    0.0803
 LZN       0.3322    0.5136    0.0574    0.5776    -.0290    -.0098    0.0803    1.0000
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APPENDIX L: Correlation matrix for New Zealand and overseas oils (16 trace elements)

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          72 Observations
          17 Variables


                                   Simple Statistics

                      LAL            LAS            LBR            LCL            LCO

     Mean     1.232797437    1.716666321    2.206224131    1.627812352    1.555049432
     Std      0.582282519    0.861727672    0.798173812    0.808616999    0.753911584


                      LCR            LCS            LEU            LFE            LMN

     Mean     2.163322192   0.9344872310   0.6014482958    1.112210114    2.134220434
     Std      0.551350173   0.3896268460   0.3441759296    0.574805442    0.607202593


                      LNA            LNI            LSB            LSC            LSM

     Mean     1.178516498   0.0675735997    1.354694817   0.2100908136   0.0865409162
     Std      0.725574042   0.6998148421    0.420041826   0.8508067651   0.7467010667


                                                LV            LZN

                                Mean   2.461104943   -.0511442519
                                Std    0.825980669   0.7087936236


                                   Correlation Matrix

              LAL      LAS      LBR      LCL      LCO      LCR      LCS      LEU      LFE

     LAL   1.0000   0.3681   0.4075   0.2605   0.3972   0.5834   0.3009   0.5017   0.6799
     LAS   0.3681   1.0000   0.4868   0.6085   0.6506   0.2538   0.0958   0.1357   0.2715
     LBR   0.4075   0.4868   1.0000   0.5859   0.5292   0.2855   0.1719   0.1906   0.3862
     LCL   0.2605   0.6085   0.5859   1.0000   0.6332   0.0295   -.0047   -.1004   0.1061
     LCO   0.3972   0.6506   0.5292   0.6332   1.0000   0.2597   0.1456   0.1490   0.3656
     LCR   0.5834   0.2538   0.2855   0.0295   0.2597   1.0000   0.4639   0.5041   0.8074
     LCS   0.3009   0.0958   0.1719   -.0047   0.1456   0.4639   1.0000   0.5297   0.3867
     LEU   0.5017   0.1357   0.1906   -.1004   0.1490   0.5041   0.5297   1.0000   0.5318
     LFE   0.6799   0.2715   0.3862   0.1061   0.3656   0.8074   0.3867   0.5318   1.0000
     LMN   0.6459   0.3338   0.3908   0.0676   0.4475   0.7594   0.4089   0.6142   0.8753
     LNA   0.5209   0.3188   0.4903   0.4386   0.4740   0.4667   0.2363   0.2506   0.5774
     LNI   0.2646   0.6718   0.5226   0.7971   0.8051   0.0863   0.0538   0.0001   0.1529
     LSB   0.4947   0.3459   0.3650   0.1667   0.3636   0.5461   0.0647   0.4402   0.5486
     LSC   0.6803   0.1755   0.2874   -.0416   0.1862   0.8140   0.3988   0.7091   0.8066
     LSM   0.6898   0.2987   0.5108   0.1088   0.3741   0.6494   0.3694   0.7100   0.7025
     LV    0.4580   0.4017   0.3518   0.4168   0.3998   0.2416   -.0079   0.0929   0.2469
     LZN   0.2116   0.5416   0.5605   0.5111   0.5714   0.3740   0.2075   0.2002   0.4322

              LMN      LNA      LNI      LSB      LSC      LSM      LV       LZN

     LAL   0.6459   0.5209   0.2646   0.4947   0.6803   0.6898   0.4580   0.2116
     LAS   0.3338   0.3188   0.6718   0.3459   0.1755   0.2987   0.4017   0.5416
     LBR   0.3908   0.4903   0.5226   0.3650   0.2874   0.5108   0.3518   0.5605
     LCL   0.0676   0.4386   0.7971   0.1667   -.0416   0.1088   0.4168   0.5111
     LCO   0.4475   0.4740   0.8051   0.3636   0.1862   0.3741   0.3998   0.5714
     LCR   0.7594   0.4667   0.0863   0.5461   0.8140   0.6494   0.2416   0.3740
     LCS   0.4089   0.2363   0.0538   0.0647   0.3988   0.3694   -.0079   0.2075
     LEU   0.6142   0.2506   0.0001   0.4402   0.7091   0.7100   0.0929   0.2002
     LFE   0.8753   0.5774   0.1529   0.5486   0.8066   0.7025   0.2469   0.4322
     LMN   1.0000   0.4640   0.2181   0.4618   0.7915   0.7659   0.3256   0.5342
     LNA   0.4640   1.0000   0.3545   0.3620   0.4112   0.4740   0.3244   0.2697
     LNI   0.2181   0.3545   1.0000   0.2283   0.0464   0.2231   0.6326   0.6087
     LSB   0.4618   0.3620   0.2283   1.0000   0.5563   0.5514   0.2158   0.2409
     LSC   0.7915   0.4112   0.0464   0.5563   1.0000   0.8420   0.3395   0.3221
     LSM   0.7659   0.4740   0.2231   0.5514   0.8420   1.0000   0.3660   0.4152
     LV    0.3256   0.3244   0.6326   0.2158   0.3395   0.3660   1.0000   0.3475
     LZN   0.5342   0.2697   0.6087   0.2409   0.3221   0.4152   0.3475   1.0000
```

APPENDIX M: Correlation matrix for New Zealand and overseas oils (6 trace elements)

```
                          Principal Component Analysis

        91 Observations
         6 Variables


                               Simple Statistics

                               LAL                 LCO                 LFE

           Mean        1.061224201         1.677794447         1.000416570
           Std         0.643984951         0.722249433         0.580495054


                               LMN                 LNI                  LV

           Mean        2.055933464        0.2881594762         2.163248099
           Std         0.599178985        0.8090924215         0.969596849


                              Correlation Matrix

                  LAL          LCO          LFE          LMN          LNI           LV

  LAL          1.0000       0.1264       0.7121       0.6438       -.0986       0.5834
  LCO          0.1264       1.0000       0.1783       0.3186       0.7609       0.0850
  LFE          0.7121       0.1783       1.0000       0.8226       -.1156       0.3820
  LMN          0.6438       0.3186       0.8226       1.0000       0.0241       0.3893
  LNI          -.0986       0.7609       -.1156       0.0241       1.0000       0.1063
  LV           0.5834       0.0850       0.3820       0.3893       0.1063       1.0000
```

APPENDIX N: Correlation matrix for New Zealand oils and bitumen

```
62 Observations
16 Variables


                                 Simple Statistics

                       LAL                 LAS                  LBR                 LCL

Mean          0.6129844750         1.031250002          1.751984728        0.9392233580
Std           0.4993553099         0.819329446          1.074024323        0.6955400059


                       LCO                 LCR                  LCS                 LFE

Mean          0.8922165053         1.607352091         0.2645357445        0.5077666543
Std           0.5616499402         0.435548019         0.2762314812        0.4564674479


                       LMN                 LNA                  LNI                 LSB

Mean           1.515882809        0.6521248465         -.8493970866        0.6525844396
Std            0.474795921        0.6991059947         0.3775281691        0.3800834179


                       LSC                 LSM                   LV                 LZN

Mean          -.2905634469        -.4908727146          1.529983245        -.7607155008
Std           0.5813131905        0.6104707056          0.462136841        0.6486322493


                                 Correlation Matrix

             LAL        LAS        LBR        LCL        LCO        LCR        LCS        LFE

LAL       1.0000     0.2265     0.1972     0.2184     0.2534     0.5682     0.1493     0.5848
LAS       0.2265     1.0000     0.6257     0.4925     0.5149     0.3990     0.0952     0.1938
LBR       0.1972     0.6257     1.0000     0.7552     0.4895     0.3112     -.1457     0.1167
LCL       0.2184     0.4925     0.7552     1.0000     0.5657     0.3354     -.0617     0.2293
LCO       0.2534     0.5149     0.4895     0.5657     1.0000     0.4579     0.0141     0.3957
LCR       0.5682     0.3990     0.3112     0.3354     0.4579     1.0000     0.3687     0.6825
LCS       0.1493     0.0952     -.1457     -.0617     0.0141     0.3687     1.0000     0.1909
LFE       0.5848     0.1938     0.1167     0.2293     0.3957     0.6825     0.1909     1.0000
LMN       0.5480     0.3428     0.1514     0.2204     0.4995     0.6563     0.2597     0.7647
LNA       0.5011     0.3613     0.5883     0.5588     0.4845     0.5786     0.0446     0.5303
LNI       0.2227     0.5506     0.5145     0.6037     0.6627     0.4237     0.1112     0.3731
LSB       0.2840     -.0105     -.2004     -.1835     0.1034     0.4886     0.4822     0.5169
LSC       0.7098     0.2347     0.3234     0.2796     0.3471     0.6371     0.1834     0.6753
LSM       0.5156     0.3608     0.5227     0.1987     0.3005     0.5102     0.0463     0.4429
LV        0.7735     0.2866     0.3422     0.3087     0.3985     0.5164     0.0457     0.5765
LZN       0.0310     0.5445     0.5620     0.5967     0.6409     0.2615     -.0033     0.3319

             LMN        LNA        LNI        LSB        LSC        LSM         LV        LZN

LAL       0.5480     0.5011     0.2227     0.2840     0.7098     0.5156     0.7735     0.0310
LAS       0.3428     0.3613     0.5506     -.0105     0.2347     0.3608     0.2866     0.5445
LBR       0.1514     0.5883     0.5145     -.2004     0.3234     0.5227     0.3422     0.5620
LCL       0.2204     0.5588     0.6037     -.1835     0.2796     0.1987     0.3087     0.5967
LCO       0.4995     0.4845     0.6627     0.1034     0.3471     0.3005     0.3985     0.6409
LCR       0.6563     0.5786     0.4237     0.4886     0.6371     0.5102     0.5164     0.2615
LCS       0.2597     0.0446     0.1112     0.4822     0.1834     0.0463     0.0457     -.0033
LFE       0.7647     0.5303     0.3731     0.5169     0.6753     0.4429     0.5765     0.3319
LMN       1.0000     0.3811     0.5063     0.4589     0.5476     0.4889     0.5819     0.4810
LNA       0.3811     1.0000     0.4134     0.2200     0.5763     0.4690     0.5407     0.3262
LNI       0.5063     0.4134     1.0000     0.1612     0.2223     0.3194     0.3834     0.7203
LSB       0.4589     0.2200     0.1612     1.0000     0.3801     0.2085     0.2506     -.0201
LSC       0.5476     0.5763     0.2223     0.3801     1.0000     0.7026     0.7232     0.1226
LSM       0.4889     0.4690     0.3194     0.2085     0.7026     1.0000     0.6304     0.3332
LV        0.5819     0.5407     0.3834     0.2506     0.7232     0.6304     1.0000     0.2719
```

APPENDIX O: Principal components analysis, New Zealand oils

```
                         Principal Component Analysis

                                Eigenvectors

             PRIN1        PRIN2        PRIN3        PRIN4        PRIN5        PRIN6

  LAL     0.317166     -.179340     -.132940     -.064148     0.069400     -.351859
  LAS     0.141582     0.176764     0.373872     -.218119     0.707138     -.314343
  LBR     0.160788     0.235557     -.430991     -.027468     0.404946     0.334686
  LCL     0.148270     0.273435     -.432975     0.508986     0.164785     -.096965
  LCO     0.226968     0.273181     0.264466     -.153090     -.251271     0.204840
  LCR     0.314654     -.141439     0.054381     -.168171     0.086942     0.376177
  LCS     0.069651     -.431812     0.150707     0.251288     0.361378     0.191323
  LEU     0.162123     -.278771     0.191306     0.619495     -.044530     -.185574
  LFE     0.355035     0.012812     -.043079     0.006190     -.068712     0.050075
  LMN     0.345675     0.114969     0.188888     -.002674     0.000118     0.006104
  LNA     0.273977     -.001724     -.401478     -.107324     -.102870     0.006371
  LNI     0.208337     0.343860     0.223118     0.263188     -.211127     -.136291
  LSB     0.265996     -.202711     0.182521     0.077378     -.053168     0.445954
  LSC     0.327910     -.219142     -.094148     -.099932     -.131890     -.088383
  LV      0.307240     -.103622     -.075685     -.266055     -.142159     -.406403
  LZN     0.114815     0.464815     0.201765     0.149197     -.020539     0.091908


             PRIN7        PRIN8        PRIN9       PRIN10       PRIN11       PRIN12

  LAL     0.044301     0.074081     0.278388     0.130146     -.012417     -.279223
  LAS     -.279040     -.054930     -.021024     -.193329     0.064125     -.075875
  LBR     0.421861     -.116636     0.419646     -.114125     -.022568     0.089036
  LCL     -.290570     0.048087     -.148675     0.261994     -.269181     -.198614
  LCO     -.025079     0.602969     0.297644     -.024956     -.208792     -.312769
  LCR     -.226392     -.035477     -.142816     0.029187     -.373301     0.544298
  LCS     0.160936     0.450119     -.074163     0.453839     0.308324     0.074575
  LEU     0.147075     0.033261     0.156167     -.567386     -.144088     0.127599
  LFE     -.040352     -.084319     -.456977     0.002553     -.008647     -.234457
  LMN     0.216373     0.043581     -.175641     -.030040     -.310792     0.062243
  LNA     -.335512     0.344380     -.072644     -.401810     0.512881     0.190234
  LNI     -.248231     -.166282     0.327558     0.355382     0.223888     0.397348
  LSB     -.222887     -.457911     0.243121     -.017381     0.249908     -.386865
  LSC     0.154540     -.185381     -.192924     0.058766     0.002477     -.122128
  LV      0.276209     -.080241     0.128400     0.196314     0.055069     0.188344
  LZN     0.431137     -.035929     -.346280     -.060817     0.385564     0.001607

            PRIN13       PRIN14       PRIN15       PRIN16

  LAL     0.487458     -.534814     -.108572     -.037378
  LAS     -.121894     0.071015     0.091092     0.075701
  LBR     -.219760     -.076199     0.030503     -.109500
  LCL     0.111980     0.278524     0.087352     0.181713
  LCO     -.115143     0.068000     0.236691     0.081501
  LCR     0.313576     -.134797     0.254585     0.099971
  LCS     -.098681     0.058947     -.028101     -.032025
  LEU     -.035961     0.015399     0.173709     -.037560
  LFE     -.267356     -.193765     0.203098     -.664660
  LMN     -.009340     0.169151     -.788156     -.027280
  LNA     0.009745     0.075329     -.190360     0.049709
  LNI     -.253091     -.227312     -.071231     -.066987
  LSB     0.174969     0.280732     -.077891     0.027756
  LSC     -.473526     -.186886     0.094341     0.646914
  LV      0.104828     0.596643     0.259663     -.149403
  LZN     0.403147     -.076295     0.182791     0.194229
```

```
                         Eigenvalues of the Correlation Matrix

                Eigenvalue      Difference      Proportion      Cumulative

     PRIN1        6.73933         3.96404        0.421208         0.42121
     PRIN2        2.77529         1.47994        0.173456         0.59466
     PRIN3        1.29535         0.33994        0.080960         0.67562
     PRIN4        0.95542         0.14365        0.059714         0.73534
     PRIN5        0.81177         0.05672        0.050736         0.78607
     PRIN6        0.75505         0.11800        0.047191         0.83326
     PRIN7        0.63705         0.14346        0.039816         0.87308
     PRIN8        0.49360         0.04135        0.030850         0.90393
     PRIN9        0.45224         0.04561        0.028265         0.93219
     PRIN10       0.40663         0.18145        0.025414         0.95761
     PRIN11       0.22518         0.08381        0.014074         0.97168
     PRIN12       0.14137         0.03058        0.008836         0.98052
     PRIN13       0.11080         0.02532        0.006925         0.98744
     PRIN14       0.08547         0.01802        0.005342         0.99279
     PRIN15       0.06746         0.01948        0.004216         0.99700
     PRIN16       0.04798          .             0.002999         1.00000
```

APPENDIX P: Principal components analysis, New Zealand and overseas oils

Eigenvectors

	PRIN1	PRIN2	PRIN3	PRIN4	PRIN5	PRIN6
LAL	0.280433	-.086557	-.272038	0.143030	0.268734	0.171642
LAS	0.210396	0.292424	0.064095	-.170866	-.149230	0.219951
LBR	0.234446	0.205380	0.064558	0.218557	-.175115	0.047462
LCL	0.157325	0.427633	0.031589	0.228995	0.017492	0.071192
LCO	0.237454	0.299310	0.095590	0.019189	-.107300	0.088166
LCR	0.275385	-.222906	0.010404	0.016613	-.090682	-.288059
LCS	0.153766	-.179032	0.663377	0.217719	0.321349	0.200092
LEU	0.218337	-.279050	0.187225	-.144943	0.070948	0.516633
LFE	0.300925	-.187797	-.034615	0.104349	-.128407	-.324323
LMN	0.306903	-.165406	0.082702	-.149509	-.036574	-.274165
LNA	0.238995	0.055548	-.139918	0.689499	0.069198	-.163167
LNI	0.192976	0.421803	0.051716	-.139706	0.152124	0.077229
LSB	0.230534	-.069208	-.369464	-.057793	-.504514	0.360484
LSC	0.285260	-.279662	-.110216	-.149456	0.074210	-.060692
LSM	0.303321	-.162182	-.055011	-.104845	0.038436	0.148254
LV	0.189282	0.197591	-.348916	-.312177	0.624397	-.122527
LZN	0.228874	0.201928	0.358671	-.344668	-.222168	-.365483

	PRIN7	PRIN8	PRIN9	PRIN10	PRIN11	PRIN12
LAL	0.083831	-.016555	-.494123	-.319987	0.353830	0.072527
LAS	0.333664	0.215076	-.549323	0.396764	-.363866	0.022062
LBR	-.676498	0.211874	-.158922	-.285313	-.283130	0.103302
LCL	-.046889	0.170898	-.000569	0.158748	0.619220	-.131990
LCO	0.294784	-.499500	0.122624	-.381176	-.156754	-.255956
LCR	0.259213	0.412132	0.091837	-.012464	-.036781	-.413670
LCS	0.163362	0.321917	0.147734	-.226447	-.109145	0.104973
LEU	-.125048	-.259079	0.118650	0.371607	0.156943	0.213407
LFE	0.128935	-.071524	-.088608	-.083881	0.145573	0.340158
LMN	0.061489	-.301870	-.146942	-.093233	-.087695	0.270466
LNA	0.031918	-.185353	0.206932	0.451904	-.219144	0.073698
LNI	0.120320	-.080718	0.276950	-.085911	0.062930	-.051839
LSB	0.131646	0.271158	0.404130	-.152553	-.002985	0.248292
LSC	-.075399	0.089724	0.042467	0.139430	0.118381	-.320507
LSM	-.347581	-.190288	-.028117	0.041963	-.142346	-.491152
LV	-.064764	0.184673	0.217783	0.018843	-.223290	0.230394
LZN	-.203610	0.016217	0.084536	0.163114	0.226564	0.131526

	PRIN13	PRIN14	PRIN15	PRIN16	PRIN17
LAL	-.346584	0.292325	-.098480	-.086149	-.103552
LAS	-.008689	-.116995	-.042283	0.027743	0.017258
LBR	0.277229	0.126951	-.139761	0.020927	-.070883
LCL	0.244112	-.169807	0.367107	0.186031	0.135305
LCO	0.073508	0.157645	-.125765	0.358492	0.252653
LCR	0.260098	0.460544	0.080164	-.257369	0.111197
LCS	-.186697	-.190926	0.070269	0.104534	-.002073
LEU	0.311451	0.327803	-.105195	-.083816	0.137132
LFE	0.200413	-.449844	-.329996	-.207334	0.415306
LMN	0.201898	-.022665	0.601320	0.072202	-.398305
LNA	-.225318	0.108417	-.027356	0.011279	-.118881
LNI	0.096887	-.149063	-.220646	-.573395	-.461246
LSB	-.212168	-.067634	0.146929	0.071253	-.048723
LSC	0.094928	-.248046	-.393808	0.502294	-.408779
LSM	-.299453	-.332610	0.281869	-.280739	0.254139
LV	0.040609	0.053485	0.079410	0.162754	0.273353
LZN	-.502010	0.242093	-.116712	0.065321	0.062055

```
                    Eigenvalues of the Correlation Matrix

            Eigenvalue      Difference      Proportion      Cumulative

PRIN1          7.61706         4.31351        0.448062         0.44806
PRIN2          3.30355         2.25490        0.194326         0.64239
PRIN3          1.04865         0.23040        0.061685         0.70407
PRIN4          0.81825         0.01628        0.048132         0.75221
PRIN5          0.80196         0.09937        0.047174         0.79938
PRIN6          0.70260         0.09820        0.041329         0.84071
PRIN7          0.60440         0.16925        0.035553         0.87626
PRIN8          0.43515         0.02633        0.025597         0.90186
PRIN9          0.40882         0.08910        0.024048         0.92591
PRIN10         0.31972         0.03889        0.018807         0.94471
PRIN11         0.28083         0.08792        0.016519         0.96123
PRIN12         0.19291         0.04339        0.011347         0.97258
PRIN13         0.14952         0.02748        0.008795         0.98138
PRIN14         0.12204         0.04162        0.007179         0.98856
PRIN15         0.08042         0.01307        0.004730         0.99329
PRIN16         0.06734         0.02055        0.003961         0.99725
PRIN17         0.04679          .             0.002752         1.00000
```

APPENDIX Q: Principal components analysis for New Zealand and overseas oils (6 trace elements)

```
                           Eigenvalues of the Correlation Matrix

                     Eigenvalue         Difference         Proportion         Cumulative

       PRIN1            2.86959            1.12754           0.478266            0.47827
       PRIN2            1.74206            0.96220           0.290343            0.76861
       PRIN3            0.77986            0.48970           0.129976            0.89858
       PRIN4            0.29016            0.12061           0.048360            0.94694
       PRIN5            0.16955            0.02077           0.028259            0.97520
       PRIN6            0.14878             .                0.024797            1.00000

                                         Eigenvectors

                 PRIN1          PRIN2          PRIN3          PRIN4          PRIN5          PRIN6

    LAL       0.509607       -.164396       0.147344       -.788346       0.006004       0.264648
    LCO       0.213502       0.660722       -.184336       -.185014       -.508042       -.437660
    LFE       0.519477       -.146339       -.342623       0.132152       0.551542       -.519303
    LMN       0.521661       -.016112       -.353934       0.455537       -.310029       0.546542
    LNI       0.056580       0.716619       0.165571       0.043542       0.568996       0.360818
    LV        0.386690       -.034679       0.821119       0.342645       -.133359       -.199603
```

APPENDIX R: Principal components analysis for New Zealand oils and bitumen

```
                                 Eigenvectors

           PRIN1        PRIN2        PRIN3        PRIN4        PRIN5        PRIN6

LAL     0.254985     0.245752     -.290854     -.009925     -.034291     0.521868
LAS     0.224676     -.259424     0.117557     0.268317     0.386136     0.214967
LBR     0.231098     -.367446     -.210542     0.301488     0.074048     -.216510
LCL     0.227781     -.357249     -.039247     0.155444     -.397334     0.151644
LCO     0.264051     -.209855     0.185927     -.199724     -.158555     0.061078
LCR     0.297502     0.172888     0.112383     0.207566     -.114565     -.054881
LCS     0.073222     0.250822     0.455710     0.585321     0.097867     0.265197
LFE     0.281627     0.240423     0.080403     -.289086     -.213243     -.133575
LMN     0.289109     0.166731     0.220353     -.349159     0.146557     0.096235
LNA     0.282976     -.035367     -.185453     0.217347     -.464939     -.270303
LNI     0.260693     -.232606     0.300391     -.132167     0.014022     0.091172
LSB     0.134533     0.387070     0.341949     0.080429     -.074882     -.395755
LSC     0.286083     0.231035     -.269438     0.084755     0.014134     -.082800
LSM     0.264628     0.069459     -.277664     0.056856     0.555372     -.389598
LV      0.288729     0.135980     -.279757     -.169413     0.100481     0.304461
LZN     0.226610     -.324571     0.276243     -.267392     0.175683     -.134383


           PRIN7        PRIN8        PRIN9       PRIN10       PRIN11       PRIN12

LAL     -.034453     0.101124     0.167895     -.032471     -.084410     0.098230
LAS     -.618925     0.043486     0.205866     0.277576     0.196431     -.142315
LBR     0.066253     -.017829     0.080764     -.047605     0.053114     0.237450
LCL     0.234560     -.204675     0.084151     -.166970     0.391521     0.231341
LCO     -.190123     0.316139     -.757850     0.076024     -.040767     0.035601
LCR     -.337024     -.244238     -.086470     -.577141     -.245873     0.196173
LCS     0.402953     -.137941     -.185903     0.204749     -.121421     -.088621
LFE     -.090835     -.389766     0.161096     0.170974     0.173671     -.359476
LMN     -.061233     -.290351     0.050739     0.027871     -.161915     0.277233
LNA     -.051781     0.111104     0.136625     0.398362     -.501751     -.159336
LNI     0.224522     0.351508     0.269602     -.440959     -.082675     -.535980
LSB     -.048615     0.495685     0.233733     0.030050     0.336059     0.332133
LSC     0.087233     -.086223     -.316418     0.026285     0.512400     -.304237
LSM     0.184165     -.019922     -.123737     -.152028     -.169423     -.075914
LV      0.238716     0.321085     0.066770     0.142046     -.030899     0.207375
LZN     0.279764     -.195693     0.071097     0.287973     -.034729     0.205443


          PRIN13       PRIN14       PRIN15       PRIN16

LAL     0.464729     0.476218     -.080008     -.098912
LAS     -.090622     -.059242     -.090533     0.133976
LBR     0.157003     -.022536     0.580544     -.434862
LCL     0.063004     -.096401     -.146928     0.490293
LCO     0.111805     0.115348     0.162846     0.107000
LCR     -.381455     0.134727     -.130933     -.127301
LCS     -.003337     0.006530     0.141586     0.031130
LFE     -.111319     0.257991     0.479223     0.161831
LMN     0.351730     -.605512     0.007394     -.050167
LNA     0.043219     -.159338     -.224936     0.020755
LNI     0.058187     -.105620     -.004636     -.109319
LSB     0.103742     0.073922     -.026833     0.051518
LSC     0.004134     -.194481     -.335807     -.395434
LSM     0.144703     0.111001     -.044277     0.492106
LV      -.626442     -.185821     0.170022     0.062013
LZN     -.153847     0.410512     -.372013     -.260820
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                    Eigenvalues of the Correlation Matrix

              Eigenvalue      Difference      Proportion      Cumulative

    PRIN1        6.97728         4.18469        0.436080         0.43608
    PRIN2        2.79259         1.28447        0.174537         0.61062
    PRIN3        1.50812         0.60470        0.094258         0.70487
    PRIN4        0.90342         0.15610        0.056464         0.76134
    PRIN5        0.74732         0.16551        0.046708         0.80805
    PRIN6        0.58182         0.11445        0.036364         0.84441
    PRIN7        0.46736         0.05226        0.029210         0.87362
    PRIN8        0.41510         0.04418        0.025944         0.89956
    PRIN9        0.37093         0.08644        0.023183         0.92275
    PRIN10       0.28449         0.02034        0.017781         0.94053
    PRIN11       0.26415         0.06962        0.016509         0.95704
    PRIN12       0.19453         0.02243        0.012158         0.96920
    PRIN13       0.17210         0.02729        0.010756         0.97995
    PRIN14       0.14481         0.04049        0.009051         0.98900
    PRIN15       0.10432         0.03268        0.006520         0.99552
    PRIN16       0.07164          .             0.004478         1.00000
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