

THE INFLUENCE OF ISORANK VARIATIONS IN VITRINITE CHEMISTRY ON VITRINITE REFLECTANCE AND SOME STERANE AND TRITERPANE MATURATION INDICATORS

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Abstract

Isorank variability in vitrinite fluorescence, reflectance, and the bulk properties of vitrinite-dominated New Zealand coals, indicates considerable variability in vitrinite chemistry, inherited from characteristics of the parent peats. Use of the term *coal type* is therefore broadened to include organic chemistry, and a Suggate plot with axes of volatile matter and specific energy is used to demonstrate type and rank trends for diverse New Zealand coals. Correction of depressed vitrinite reflectance in high volatile type coals to "average type" reflectance is explained, using a technique which requires information from a Suggate plot and a graph relating vitrinite reflectance to volatile matter. Coals from Tara-1 (Great South Basin) and Ohanga-1 (Taranaki) exemplify correction of reflectance for type and for variation in moisture resulting from differences in geothermal gradient.

Effects of coal type on petroleum source potential are evaluated using GCMS analysis of well characterised serial sample suites from West Coast (South Island) coalfield exploration programmes. All but one of the six determined biomarker ratios exhibit substantial dependence on type as well as rank variation. The C31/C30 hopane ratio exhibits least type dependence, and declines with increasing maturity to a minimum value just below 1.0, at high volatile bituminous A rank, after which it is no longer sensitive to maturity changes. In contrast, C29/C30 hopane, and C29 and C30 moretane/hopane ratios show an expected decline with increasing maturity, but begin to rise again at high rank, possibly indicating expulsion of oil. Serial sample trends suggest that high volatile type coals may mature and expel at lower temperatures than low volatile type coals of equivalent thermal history. The % $\beta\beta$ sterane ratio shows the expected increase with increasing maturity, becoming insensitive to changes above high volatile A bituminous. The $\alpha\alpha$ /C29 S/S+R sterane ratio is very scattered and provides no significant indication of maturity for the West Coast samples.

Introduction

There appears to be general agreement, based on stratigraphic and geochemical data, that petroleum in the Taranaki and Westland basins has been sourced from Cretaceous to Eocene terrestrial and paralic sequences. Therefore, an understanding of variability in composition of terrestrial organic matter, including coals, is a prerequisite for evaluation of source potential. Similarly, there is a need for common ground between traditional coal characterisation and concepts of petroleum generation and chemistry. This paper attempts to link these disciplines via application of biomarker geochemistry to well characterised coal samples obtained during coalfield exploration. Coals are more diverse than is generally recognised, and there is still a tendency to think in simple terms of three maceral groups (vitrinite, liptinite, inertinite) and assume that the humic (vitrinite) component will always be consistent in character. Also, liptinites are sometimes still regarded as key source materials because of

their high hydrogen content, when in fact the volumetrically more abundant vitrinite may be of equal or greater importance. Sterane and triterpane (hopane) geochemical biomarkers are used here to provide further information on the generation of petroleum hydrocarbons from New Zealand coals.

Type, Rank, and Maturity

Previous work has demonstrated that New Zealand coals exhibit considerable variability in bulk properties which cannot be explained in terms of maceral group proportions or burial history (Suggate, 1959; Suggate & Lowery, 1982; Newman, J. & N.A. 1982; in press). Some adaptation and refinement of the term "type" is therefore necessary, as defined below along with clarification of other terms used in this paper.

coalification: progressive change in coal properties in response to increasing pressure and temperature during burial.

rank: the degree of coalification. Suggate (1974) distinguishes chemical rank (thermal effects on coal chemistry) from physical rank (pressure effects on moisture via changes in coal porosity).

isorank: samples with the same coalification history

serial samples: adjacent samples, or samples in very close stratigraphic proximity, which consequently have the same burial history and are therefore isorank

type (conventional): composition in terms of macerals (microscopic organic constituents, i.e., vitrinite, liptinite, inertinite)

type (as used by Suggate, and Newman): any compositional features or variations of the organic coal substance which cannot be attributed to burial history and are therefore inherited from the parent peat. For example, New Zealand coals exhibit isorank variations in hydrogen, volatile matter, and vitrinite reflectance, and a coal may be referred to as being of a "high volatile type"*

perhydrous vitrinite: vitrinite unusually rich in hydrogen and exhibiting depressed reflectance in comparison to more typical vitrinites with the same thermal history. A coal comprising perhydrous vitrinite will have high volatile matter in relation to rank, even if liptinite is sparse, and herein is referred to as being of "high volatile type"*

***high volatile bituminous:** this is a coal rank term, for coals intermediate between sub-bituminous and medium volatile bituminous ranks (Figure 1). Care is needed to avoid confusion with "high volatile type", which has a completely different meaning (above).

maturity: concepts of maturity are not well standardised, but for the purpose of this paper a mature coal has approached peak hydrocarbon generation, although expulsion may not have occurred. Maturity may be attained at different temperatures by different materials and is a function both of inherent type characteristics and rank attained as a result of coalification.

volatile matter: during "proximate analysis" of coals, volatile matter is determined as the weight lost during heating of a sample at c. 900°C in the absence of oxygen (after first driving off free moisture at c. 100°C).

specific energy: the heat produced on combustion.

dry mineral matter and sulphur free (dmmSf): after mathematical correction for contributions made by organically bound sulphur and thermally unstable minerals. The complexity of correction formulae depends on their responsiveness to the mineral matter assemblage of individual

samples (e.g., Newman, N.A. 1985). The following general formulae are applicable to coals with less than 10 % ash.

$$\text{Volatile matter dmmSf} = \frac{100(\text{VM} - 0.1\text{A} - 0.5\text{S})}{100 - 1.1\text{A} - \text{S}} \quad \text{all dry basis}$$

$$\text{Specific energy dmmSf} = \frac{100(\text{SpE} - 0.095\text{S})}{100 - 1.1\text{A} - \text{S}} \quad \text{all dry basis}$$

where VM = volatile matter, A = ash, S = sulphur, SpE = specific energy, in Megajoules/kg (MJ/kg).

Dry basis can be determined by:

$$\text{X dry basis (db)} = \frac{\text{X} \times 100}{100 - \text{Moisture}}$$

These formulae are those generalised for New Zealand coals by Suggate (1959), except that only half of the sulphur is considered to report in the volatile matter (e.g., Parr, 1904; Newman, N.A. 1985). To convert from British Thermal units (BTU/lb) to MJ/kg: 1 BTU = 0.002326 MJ. If using BTU, the numerator for specific energy dmmSf is 100(SpE-40S).

An understanding of petroleum generation from coals therefore depends on an understanding of controls on coal type. This requires a method by which the influence of coal type and rank on coal properties can be differentiated. This is most simply achieved in the case of isorank serial samples, between which any organic differences can be attributed to type variation, according to the usage of Suggate or Newman. For coals with differing burial histories, comparison of type can be achieved using Suggate's system for rank assessment. In this system the influence of type on coal properties is accommodated by "isorank lines" on a bivariate plot of volatile matter and specific energy (Figure 2), or alternatively hydrogen and carbon (Suggate, 1959). The isorank lines are abstractions based on empirically demonstrated linear relationships for serial samples of varying type. All variables are expressed on a mineral and sulphur free basis, and the coalification path of a theoretical, relatively low-volatile type coal is shown as a line of "average type". Suggate (1959) defined this line in the context of coals worldwide, most of which have lower volatile type than New Zealand examples, so the average-type line is in fact "below" average by New Zealand standards. Although the validity of this and all other rank assessment techniques is difficult to test for coals of varying type from different coalfields (Newman & Newman 1982, 1983; Suggate & Lowery 1982, 1983), the Suggate scheme is useful and is adopted here primarily as a means of quantifying type variation (Newman, J. 1989; Newman & Newman, in press). Given that most type variation in high volatile bituminous (Figure 1) coals is manifest as displacement along isorank lines of generally consistent orientation, a new type parameter, delta volatile matter (dVM, Newman, J. 1989; Newman & Newman, in press), can be defined. This is expressed as the difference between measured volatile matter and the theoretical volatile matter of a sample of equal rank but "average" type (Figure 2). This parameter cannot be readily applied to coals of higher rank than high volatile rank or high volatile bituminous because isorank lines depart from a uniform linear orientation at high ranks. The use of volatile matter instead of hydrogen is favoured for two reasons. Firstly, it is cheaper to determine than hydrogen and is much more widely available. Secondly, the repeatability and reproducibility of hydrogen measurements are poor

Rank	Reflectance (mean maximum %)
sub-bituminous	<0.47
high volatile bituminous C	0.47 - 0.57
high volatile bituminous B	0.57 - 0.71
high volatile bituminous A	0.71 - 1.10
medium volatile bituminous	1.10 - 1.50
low volatile bituminous	1.50 - 2.05
semianthracite	2.05 - 3.00
anthracite	>3.00 (approx)

Figure 1: Coal rank classification related to vitrinite reflectance (from Ward, 1984). The ranges indicated are informal and approximate. Some coals fall outside the indicated extremes.

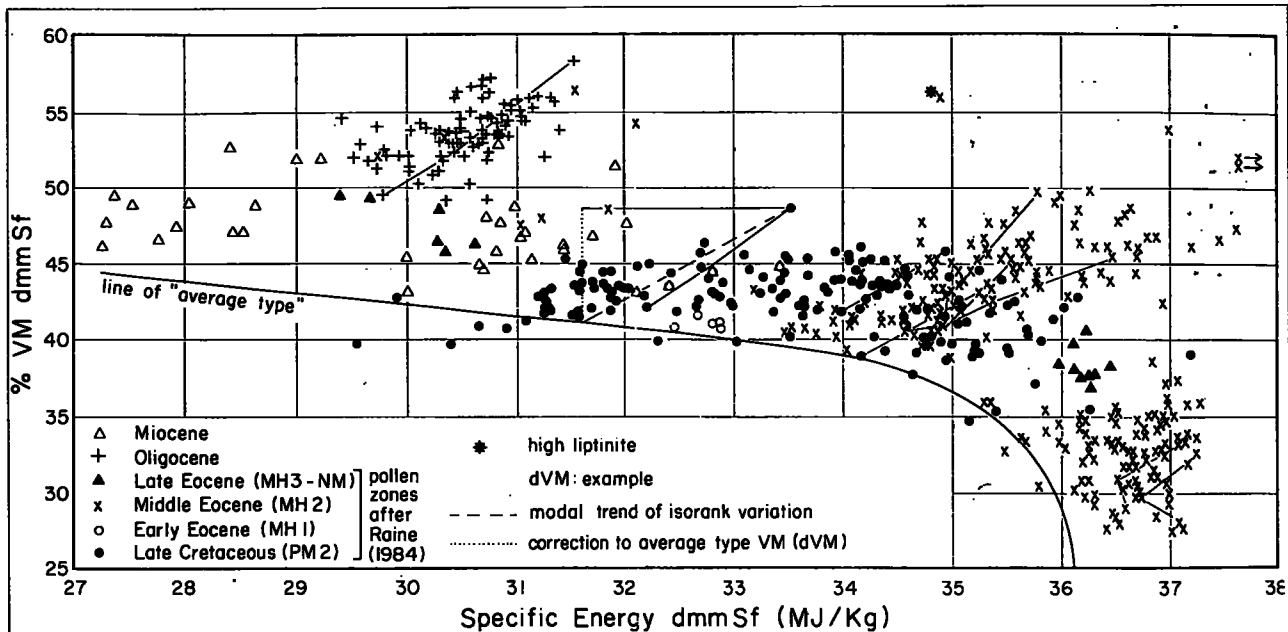


Figure 2: Cretaceous and Tertiary New Zealand coals, plotted on axes of volatile matter and specific energy (the "Suggate plot"). The significance of the line of "average type", and derivation of dVM, are discussed in the text.

compared with volatile matter (Table 1). Nevertheless, for those not accustomed to Suggate plots, Figure 3 provides a van Krevelen diagram showing the position of the New Zealand coal band, and the range of HC/OC values demonstrated by some middle Eocene coals.

Vitrinite Chemistry

Considerable evidence has accumulated indicating that isorank chemical variation in many important New Zealand coals is a consequence of variability in vitrinite chemistry. This is most directly indicated by isorank variation in average vitrinite reflectance and fluorescence between serial plies (Newman, 1987, 1989; Quick & Moore, 1991). Also, in coals comprising >90 % vitrinite, large variations in bulk properties such as volatile matter and hydrogen must be attributed to variation in vitrinite composition. Further, some middle Eocene coals with only a few percent liptinite have higher volatile matter than relatively liptinite rich coals of equivalent rank.

As stated previously (Newman & Newman, 1982), variation in vitrinite chemistry often cannot be explained in terms of the vitrinite (tissue) versus B (matrix) concept. All vitrinite submacerals are affected in many New Zealand coals with depressed reflectance (Figure 4). A simple measure of relative proportions of vitrinite A and B is the tissue preservation index (TPI) of Diessel (1984), adapted to a total vitrinite basis. Figure 5 shows relationships between dVM and TPI for a wide range of New Zealand coals, with fields distinguished in terms of age. Middle Eocene (most Brunner Fm and some Kapuni Group) coals have very low TPI (high proportions of matrix, but little tissue) irrespective of volatile matter, which ranges extremely widely from dVM 0: to 15 %+. Cretaceous coals sometimes exhibit "conventional" relationships whereby high TPI coals have relatively low dVM, whereas some latest Eocene/early Oligocene coals with very high TPI (up to 4.0) have high dVM compared with equivalent low TPI samples (Newman, 1989). Isorank variation in vitrinite chemistry is expected to influence

	hydrogen	volatile matter
Determined value for example	5.5 %	42.5 %
Repeatability as % absolute	0.1	0.3
Repeatability as proportion of sample	1.8 %	0.7 %
Reproducibility as % absolute	0.5	1.0
Reproducibility as proportion of sample	9.0 %	2.4 %

Table 1. Repeatability and reproducibility of hydrogen versus volatile matter (Australian and British Standards).

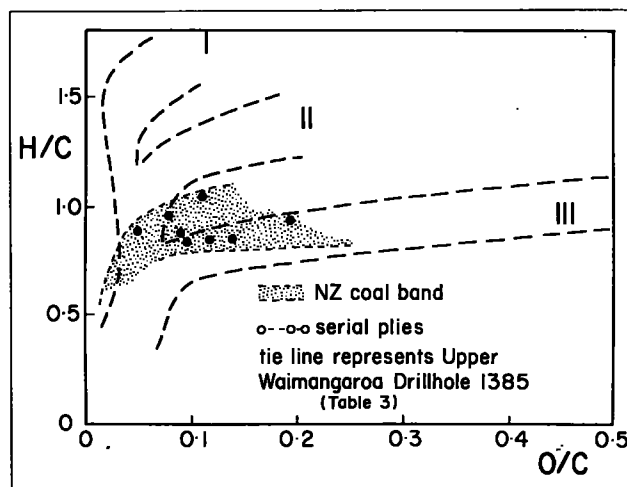


Figure 3: The New Zealand coal band on axes of atomic H/C and O/C ratio. Plotted points demonstrate the range of compositions exhibited by some New Zealand coals of middle Eocene age.

source potential and maturation rates of coals (Newman & Newman, 1982; Newman, 1989), as discussed in the context of GCMS data later in this paper.

Interpretation of coal properties in terms of depositional setting indicates that hydrogen-rich (perhydrous) vitrinites result from peatification under particularly anoxic and, in extreme cases, brackish conditions, as proposed by Teichmüller (e.g., 1975). These controls are consistent with paleoenvironmental evidence for variation in mire regime during particular time intervals. However, major differences in TPI and dVM ranges for coals of different ages but apparently similar depositional (sedimentary) regimes suggests the influence of climate and/or flora. Therefore, a more complete understanding of controls on coal properties and source potential awaits clarification of paleoecology and paleoclimate variations for Cretaceous and lower Tertiary

sequences. Daniel (in prep.) has undertaken physiognomic analysis of Middle Eocene megaflora from several West Coast sites and initial results indicate high temperatures and rainfall, which may have relevance to the unusual characteristics observed for coals of this age. It is not yet clear whether the important effect is high temperature during peatification, or abundance of a particular plant assemblage favoured by high temperatures.

There is a variety of evidence that the chemistry of particularly perhydrous New Zealand vitrinites is influenced by the presence of submicroscopic liptinite constituents. Firstly, coals which are liptinite-poor but have high dVM plot in the same position on a volatile matter/specific energy plot as very liptinite-rich (30%+ liptinite) coals of equivalent rank. Secondly, TEM studies of Brunner coals at the Australian National University (e.g., Taylor, 1991) have identified sub-micron sized lipid bodies considered to be of bacterial origin. Bacterial lipids are attributed to Type I and II kerogen, hence vitrinites incorporating lipids of this character may be important source materials, and could conceivably mature earlier (i.e., at lower temperatures) than humic coals lacking this material.

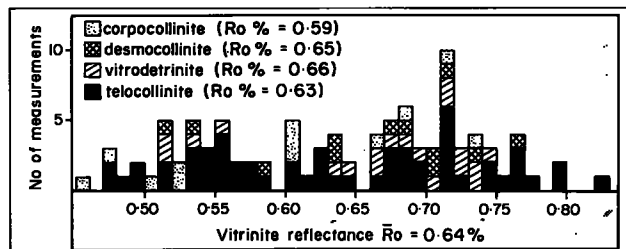


Figure 4: Reflectance histogram for a middle Eocene Ohanga-I coal sample (Coal Research Association sample 46/891), in which all vitrinite submacerals have similar reflectance ranges and means.

Use of dVM to Correct Vitrinite Reflectance to Average-Type Basis

In the case of high volatile type coals with depressed vitrinite reflectance, determination of average-type volatile matter

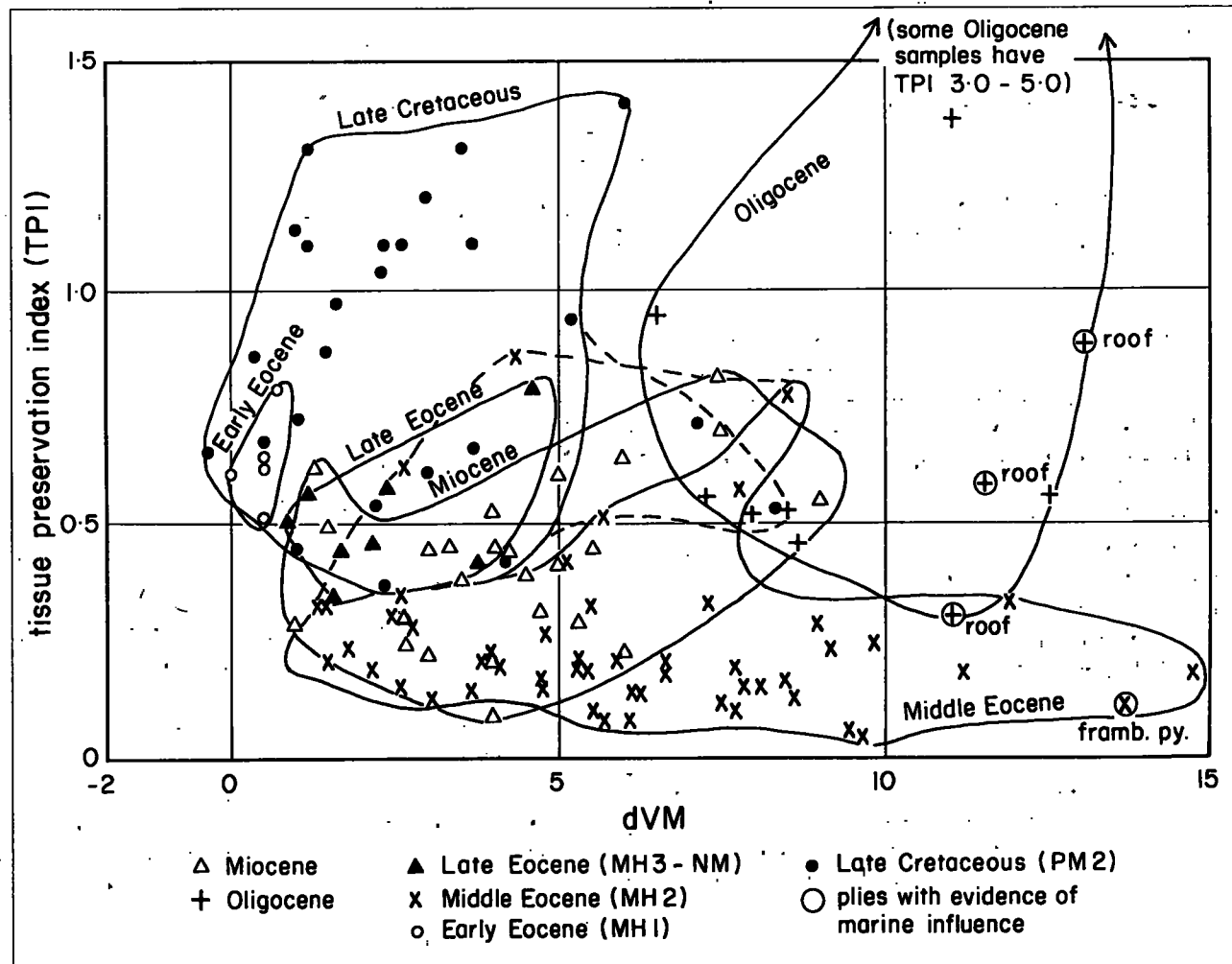


Figure 5: Plot of tissue preservation index against dVM, showing ranges for coals of various ages. Pollen zones are from Raine (1984).

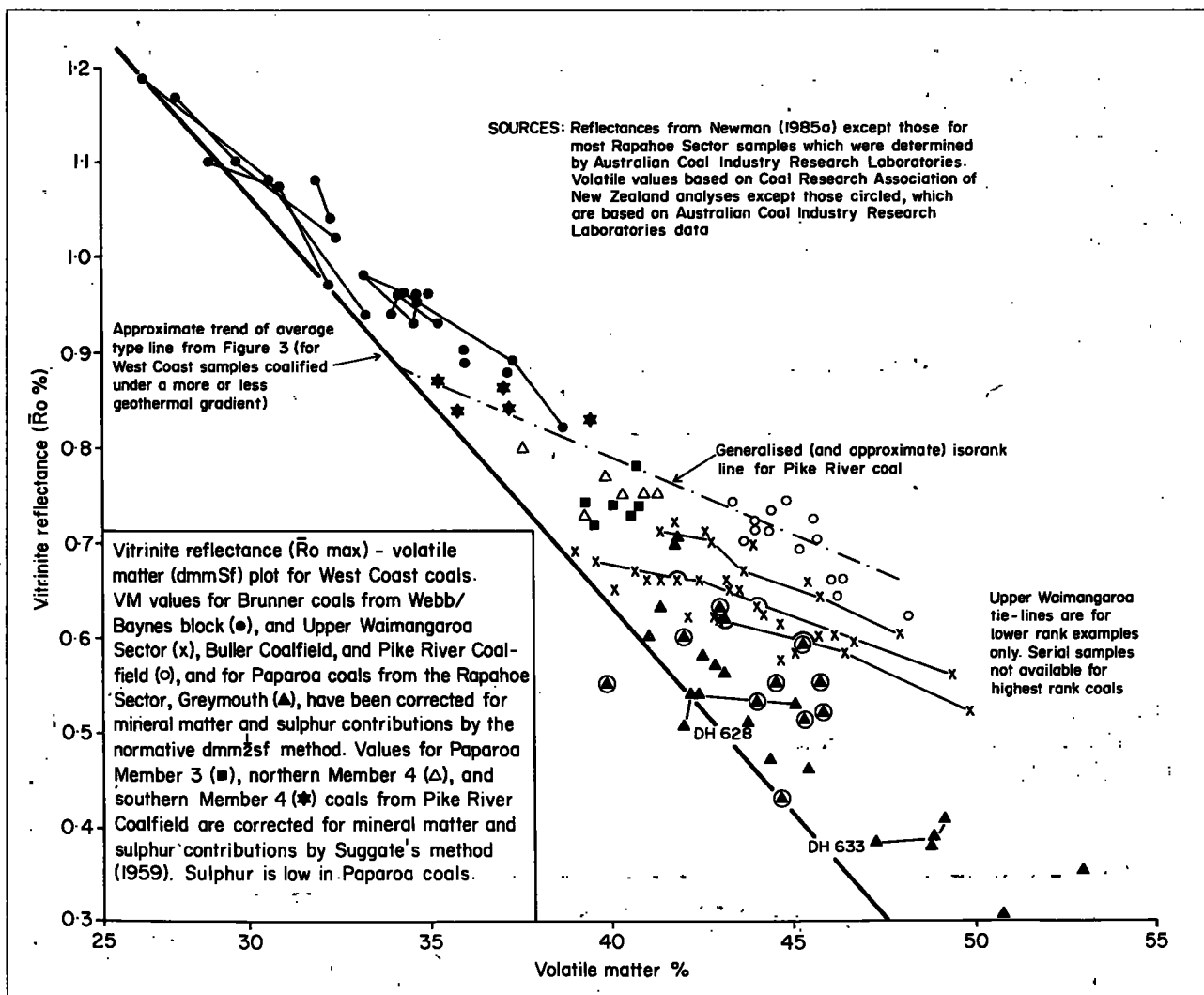


Figure 6: Relationship between vitrinite reflectance and volatile matter for West Coast coals, showing the empirically determined position of the average type line from Figure 2.

permits estimation of reflectance for a "normal" coal of equivalent rank. Firstly, the average-type line on the Suggate plot (Figure 2) defines which coals have average type. These coals then empirically dictate where the average-type line falls on a plot of reflectance and volatile matter (Figure 6). For a sample of high volatile type, determine the theoretical average-type volatile matter on the Suggate plot (Figure 2), and read off the corresponding average-type reflectance on Figure 6. Alternatively, the isorank line for a suite of serial samples plotted on Figure 6 can be extrapolated to intersect the average-type line, where the average-type reflectance value is read off. Either technique is useful, particularly for middle Eocene coals of high volatile bituminous rank, for example Kapuni Group coals near the bottom of the Ohanga 1 well (Figures 7 & 8). A suite of Lower Eocene Kapuni Group coal samples from around 3500 m in Kapuni-8 are plotted for comparison. These samples are of "average type" according to the Suggate plot (Figure 7). Correction of vitrinite reflectance values should therefore not be necessary, and this is confirmed by Figure 8 on which the Kapuni-8 samples plot close to the average-type reflectance/volatile matter line. It should be noted that not all high volatile samples have perhydrous vitrinite with depressed reflectance. Occasional samples of both Cretaceous and Eocene coals

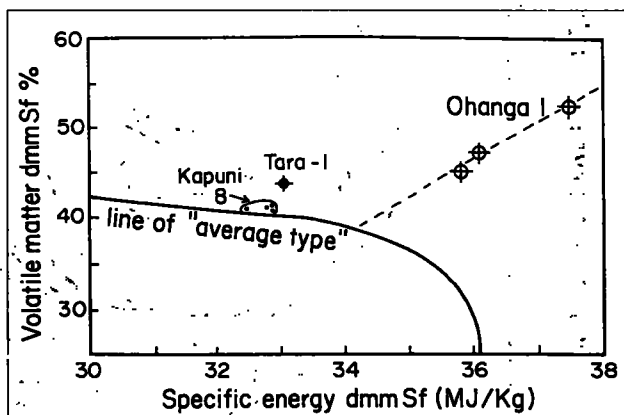


Figure 7: Ohanga-1, Kapuni-8, and Tara-1 coals on a Suggate plot.

have "average type" vitrinite, but high volatile matter due to abundant liptinite. These coals will exhibit approximately the same measured reflectance as that calculated via Figures 2 and 6. Samples with abundant inertinite (rare, and usually restricted to the Cretaceous and Paleocene) are not expected to conform to Figures 2 and 6, due to the low volatile content of most inertinite macerals.

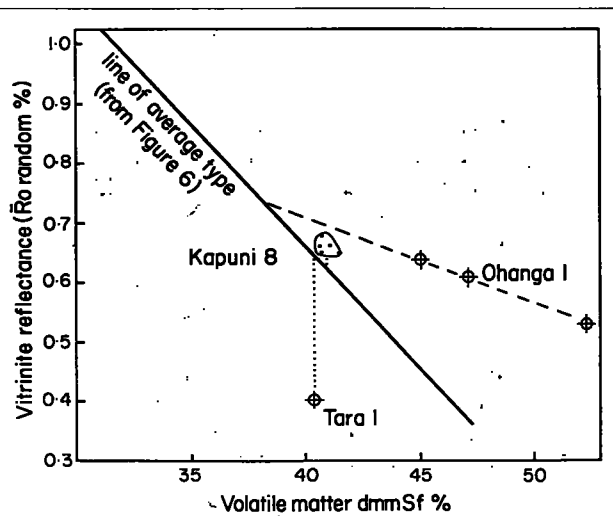


Figure 8: Determination of average type reflectance (1) for high volatile type coals with perhydrous vitrinites of low reflectance (e.g. Ohanga-1), and (2) for coals with unusually high moisture, hence low reflectance, caused by coalification under a high geothermal gradient (e.g. Tara-1).

As explained by Suggate (1974), coals which have attained the same burial temperature (hence chemical rank) under different geothermal gradients will have different moisture contents, and therefore different physical rank. This is because greater burial is required to attain a particular temperature when the geothermal gradient is low, and this extra loading reduces porosity and moisture content. As Suggate and Lowery (1982) demonstrate, given the same chemical rank but different physical rank, low moisture coals have higher reflectance than higher moisture coals. This therefore influences estimation of "average type reflectance" from chemical rank. The problem and a possible solution are demonstrated by coals from Ohanga-1, Kapuni-8, and a Great South Basin sample from Tara-1 (Suggate & Lowery, 1982). A average-type volatile matter for the Ohanga suite on the Suggate plot of volatile matter and specific energy is 38 % (Figure 7), and on the reflectance/volatile matter plot (Figure 8) the Ohanga isorank line again intersects the average-type line at 38 % Volatile matter, specific energy and reflectance are also in agreement for the Kapuni-8 samples. These relationships suggest that the Ohanga and Kapuni-8 samples have coalified under a similar geothermal gradient to the West Coast samples (discussed later in the paper), on which the reflectance/volatile matter average-type line (Figures 6 and 8) is based. On the other hand, the Tara-1 coal, which has 45 % volatile matter (dmmSf) and falls a little above the average-type line on the Suggate plot, lies well below the line of average type on the reflectance/volatile matter plot (Figure 8). That is, their reflectance appears much too low for their chemical rank, as pointed out by Suggate and Lowery (1982). This relationship indicates that the Tara-1 sample has coalified under a higher geothermal gradient than the West Coast and Taranaki samples cited here, and consequently has a relatively high moisture and low reflectance in relation to its chemical rank. To adjust the Tara-1 reflectance to average type on the same basis as the West Coast and Taranaki samples; read off, on the average-

type line (Figure 8), the reflectance value corresponding to their average-type volatile matter. The resulting value is a little under 0.70 %, substantially higher than the measured value at approximately 0.4 %.

General application of this method obviously requires standardisation of a reference average-type line on the volatile matter/specific energy plot, which in this case is Suggate's original line. Because the range of unweathered New Zealand coals which actually fall as low as this line is limited, definition of the corresponding average-type line on Figure 6 lacks precision. An alternative average-type line on the Suggate plot could be defined, for example at dVM = 2% in relation to the present line. Whichever average type line acts as the reference on the Suggate plot (Figure 1), the samples selected to translate the line onto the reflectance/volatile matter plot must have all accumulated under a *more or less common geothermal gradient*, otherwise they will not conform to a uniform reflectance/volatile matter relationship. The West Coast coals used to define the reflectance/volatile matter line in Figure 6 and 8 appear to meet this important criterion. However, further consideration of samples from petroleum wells is needed to determine how appropriate this "West Coast" line is, in the context of petroleum exploration. To summarise, any reference average-type line can be adopted for Figure 6, provided it is transferred from the volatile matter/specific energy plot via a suite of samples coalified under a common geothermal gradient.

GCMS Biomarkers as Indicators of Maturity

Introduction

Organic biomarkers can provide valuable information on maturation, source provenance, oil-oil and oil-source rock correlations in the process of petroleum generation. This information is obtained from a consideration of the various sterane and triterpane (hopane) biomarker compounds. A detailed discussion of the particular biomarkers used and their respective ratios together with an interpretation of some Taranaki data are given elsewhere (e.g., Johnston *et al.* 1988, Johnston & Collier 1991, Johnston *et al.* this issue). Research undertaken at the Chemistry Department and School of Earth Sciences, Victoria University, under the leadership of Dr Jim Johnston, has demonstrated that a variety of biomarkers can be used to define downhole increases in maturity of coals, and to predict the probable depths at which most oil has been produced. During 1988 and 1989 Canterbury Coal Research Group (CCRG) provided a suite of 34 West Coast coal samples for analysis by P. Lake, a postgraduate student working under Dr Johnston (Lake, 1989). This sample set comprised suites of serial plies from 13 seam intersections, from Cretaceous and Eocene sequences at Greymouth, Pike River, and Buller Coalfields (Table 2). The importance of these samples is their range of both type and rank, which have been well defined by existing studies. Coals of the same age and character occur elsewhere within the Westland Basin, and in the Taranaki Basin. It must be stressed that the type variation referred to in this context is principally related to variation in vitrinite chemistry. Liptinite-rich samples with average-type vitrinite will also have high volatile matter, but will not have the same organic chemistry as a high volatile liptinite-poor sample of equivalent rank containing perhydrous vitrinites.

Coal Research Association sample number	Drillhole	Formation	Site	Region
35/763-766	1281	B	Upper Waimangaroa	Buller Coalfield
39/315-318	1385	B	Upper Waimangaroa	Buller Coalfield
35/767-769	1334	B	Upper Waimangaroa	Buller Coalfield
31/083-085	1222	B	Stockton-Webb	Buller Coalfield
31/110-112	1241	B	Stockton-Webb	Buller Coalfield
31/044-048	1215	B	Stockton-Webb	Buller Coalfield
30/926-928	PRDH2	B	Pike River Coalfield	Inland Punakaiki
33/045, 30/971, 985	PRDH6	B	Pike River Coalfield	Inland Punakaiki
30/150, 151, 153	outcrop	B	Pike River Coalfield	Inland Punakaiki
27/528, 531, 522	outcrop	P	Pike River Coalfield	Inland Punakaiki
44/080-082	old mine	P	Liverpool #3 intake	Greymouth Coalfield

Table 2: Stratigraphic and geographic information for the West Coast coal sample suite. Pike River outcrop locations are described by Newman and Newman, 1991. Coalfield drillhole sites are on record with the Energy and Resources Division (Ministry of Commerce).

Results and discussion

Extraction technique and analytical methods are described by Johnston *et al.* (1988). Biomarker ratios determined by Lake (1989) are listed in Table 3, together with volatile matter, specific energy, reflectance, and sulphur data. Figures 9 to 14 present each particular biomarker ratio in relation to volatile matter, and respective serial plies are defined by tie-lines. With respect to the definitions provided earlier, chemical variability along tie-lines, i.e., between serial samples, is attributed to the effect of variation in original peat composition. A bivariate plot in this form therefore permits interpretation of biomarker data in terms of both rank (which displaces the tie-lines) and type effects. Before these controls are assessed, however, it is useful to consider (a) how much of the variability in biomarker values may result from experimental uncertainty, and (b) how closely the biomarker extracts correlate with bulk properties of the coals.

In Figures 9 to 14 two pairs of Upper Waimangaroa (Buller) coals are defined by envelopes. These samples are two adjacent plies from Drillhole 1281 (samples 35/765 and 766), and two adjacent plies from Drillhole 1385 (samples 39/315 and 316). The individuals within each pair have very similar bulk properties as indicated by volatile matter. Their close association for each particular biomarker ratio indicates good correspondence between extract composition and bulk chemistry, and good experimental precision, with respect to both extraction/measurement, and subsequent integration of the appropriate peaks in the experimental GCMS mass fragmentograms. However, the scatter of other samples, and particularly the frequent lack of a consistent linear relationship between biomarker values and volatile matter for serial plies, indicates some as yet unexplained complexity.

Figures 9 to 14 demonstrate a variety of effects of rank and type on biomarker values. Previous work on materials of rather uniform type has defined generally well-behaved variations in biomarker ratios, related principally to depth and, therefore, burial history (e.g., Johnston *et al.* 1988). The West Coast suite, by contrast, is more heterogeneous with respect to type and this is reflected by the substantial

variation in ratio values, even between serial samples known to have the same burial history. Also, the suite includes post-mature samples which allow assessment of compositional trends at high rank. The C29/C30 hopane, C29 moretane/hopane, and C30 moretane/hopane ratios exhibit dependence on type and rank variation, and an intriguing reversal of values at high volatile A bituminous rank. These ratios have been demonstrated to decrease with increasing maturation (Johnston *et al.* 1988, Collier & Johnston, 1991), and a reversal at high rank has not previously been shown. The C31/C30 hopane ratio is principally related to rank, but reaches a maximum just below C31/C30 = 1.0, at high volatile A bituminous rank, after which it is no longer sensitive to rank increase. The $\alpha\beta\beta$ sterane ratio shows good differentiation in terms of both type and rank, but reaches a maximum of around 0.5 at high volatile A bituminous ranks and, like the C31/C30 hopane ratio, is insensitive to further coalification. Finally, the $\alpha\alpha$ S/S+R ratio values appear strongly type dependant, and very insensitive to rank variation in the West Coast suite, even though Collier and Johnston (1991) have previously shown that both this and the $\alpha\beta\beta$ ratio demonstrate a good relationship with maturation in Taranaki coals, increasing to a maximum of c.0.5 for mature samples.

The diversity of trends suggests that different biomarkers are sensitive to different aspects of the coals. The reversal of C29/C30 hopane, and C29 and C30 moretane/hopane ratio values in coals approaching medium volatile bituminous rank (Figures 9 to 11), suggests differentiation of the coal into oil and residual coal fractions during maturation, followed by expulsion of the oil, which has conferred the "mature" signature. This scenario indicates partitioning of molecular species between the oil and the coal from which it has been sourced. The C29/C30 hopane, and C29 and C30 moretane/hopane ratios are therefore (hypothetically) responding to the presence of oil, which suggests that their relationship with type variation results from recognition of the amount of oil which a submature sample has generated (but retains for some time, according to Johnston *et al.* 1988). The implication here is that different coals generate different amounts of oil at any particular temperature, and possibly

Lake Data										
Sample CRA #	C2930hop	C3130hop	C30mor/hop	C29mor/hop	C29aaaS	%BBS	volatile matter %	specific energy	Ro% vitrinite	sulphur
35/763	.84	1.8	.24	.2	.52	.37	49.7	35.79	.56	4.47
35/764	.95	1.71	.24	.15	.48	.33	42.6	34.98	.66	3.03
35/765	.91	1.7	.41	.29	.44	.22	40.7	34.48	.67	.80
35/766	.9	2.03	.44	.31	.45	.21	41	34.93	.66	.57
39/315	.89	1.79	.46	.46	.36	.23	47.4	not avail	.55	4.51
39/316	.89	1.87	.44	.45	.38	.24	46.5	34.70	.59	1.84
39/317	.91	1.92	.54	.5	.36	.19	39.5	34.05	.64	.45
39/318	.94	1.66	.51	.42	.45	.2	41.7	34.55	.64	.47
35/767	.83	1.88	.31	.3	.42	.29	43.5	35.37	.62	2.25
35/768	.9	2.02	.17	.17	.44	.38	49.9	36.27	.52	5.00
35/769	.83	2.52	.17	.23	.43	.39	46.5	36.19	.68	4.90
31/083	.89	.96	.14	.18	.52	.5	32.6	37.23	1.02	2.81
31/084	.83	.97	.12	.07	.55	.5	29.7	36.71	1.10	1.14
31/085	.78	.98	.14	.06	.5	.5	28.1	37.08	1.19	3.78
31/110	.88	.63	.41	.33	.49	.56	33.3	35.67	.94	3.55
31/111	.84	1.04	.23	.25	.41	.55	30.5	36.97	1.08	1.14
31/112	.87	.75	.13	.14	.44	.55	27.5	37.03	1.19	3.83
31/044	.54	.81	.18	.1	.5	.51	38.6	36.83	.82	4.15
31/048	.56	.69	.23	.13	.44	.54	33.2	36.46	.98	2.60
30/926	.74	1.38	.12	.12	.42	.43	46.6	**	.78	8.12
30/927	.67	.75	.08	.11	.38	.37	48.7	36.64	.62	2.79
30/928	.64	.8	.12	.07	.36	.36	44.8	35.61	.73	.84
33/045	.65	.84	.13	.07	.31	.32	44	36.45	.70	.64
30/971	.58	1.07	.09	.14	.42	.43	47.5	37.62	.66	6.32
30/985	.62	.71	.09	.1	.39	.4	45.6	36.71	.69	2.34
30/150	.67	.9	.09	.11	.51	.46	53.7	37.00	.53	7.28
30/151	.77	.92	.11	.1	.5	.47	47.8	35.60	.63	3.20
30/153	.81	1.03	.28	.13	.47	.39	43.9	34.50	.72	0.72
44/080	.84	1.05	.12	.09	.58	.46	37.6	35.72	not avail	.33
44/081	.74	1.21	.13	.04	.55	.53	36.2	35.32	.81	.24
44/082	.63	1.28	.16	.09	.57	.46	35.8	35.48	.75	.27
27/528	.87	.59	.11	.05	.54	.51	34.8	36.26	.99	1.26
27/531	.72	.75	.1	.07	.47	.37	39.4	37.19	.83	.36
27/522	.89	1.27	.34	.2	.41	.24	40.5	35.45	.73	.44

** ash too high for accurate correction to dmmSf basis

Table 3: Coal Research Association (CRA) sample numbers relate to the National Coal Database. Volatile matter and specific energy are expressed as dry mineral matter and sulphur free according to individualised mineral correction formulae of N.A. Newman (1988) or, in the absence of geochemical data, according to the generalised formulae provided in the text. Sulphur is on an air-dried basis, not corrected for moisture or mineral matter. Biomarker ratio data are from Lake (1989).

overall. In contrast, the C31/C30 hopane ratio apparently perceives no difference between the oil and the coal left behind, because this ratio neither responds to type, nor exhibits a reversal in value at high ranks when the other hopane ratios indicate oil expulsion. Unfortunately, this ratio also stops differentiating between coals of different maturity before peak petroleum generation is achieved, at least in the case of the West Coast suite.

With respect to Figures 9 to 11 it is interesting that in the case of the submature to mature Upper Waimangaroa and Pike River coals, an increase in volatile matter within an isorank suite of serial plies often corresponds with increasing maturity (declining ratio value). This trend is not invariable—often there is no significant change in biomarker ratio value—but few increases in volatile matter are accompanied by a significant *decline* in maturity. Conversely, the mature to

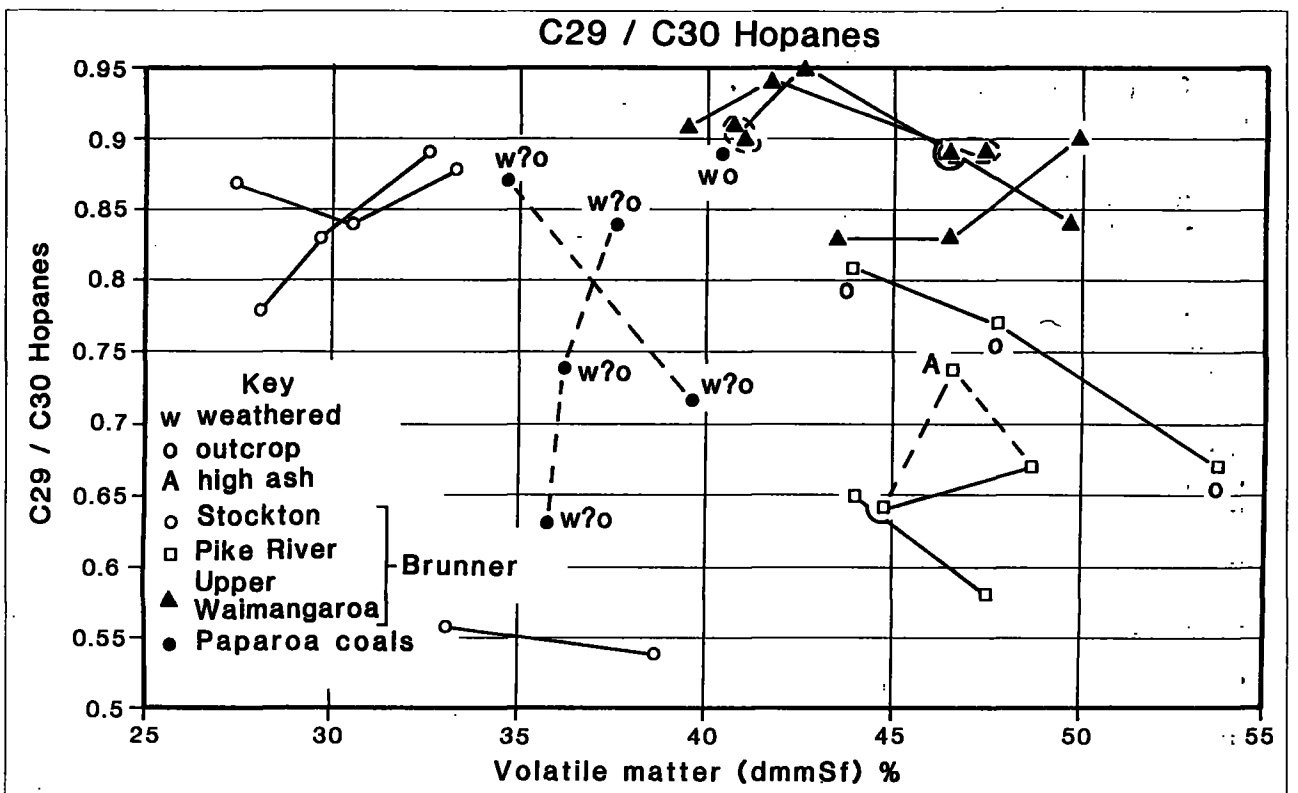


Figure 9: C29/C30 hopane ratio values plotted against volatile matter for West Coast coals. Tie-lines link isorank serial samples. Although the hopane (triterpane) biomarker ratios in Figures 9 to 11 are conventionally considered to decline with increasing maturity, Stockton coals with high ratio values have significantly higher rank than the other samples.

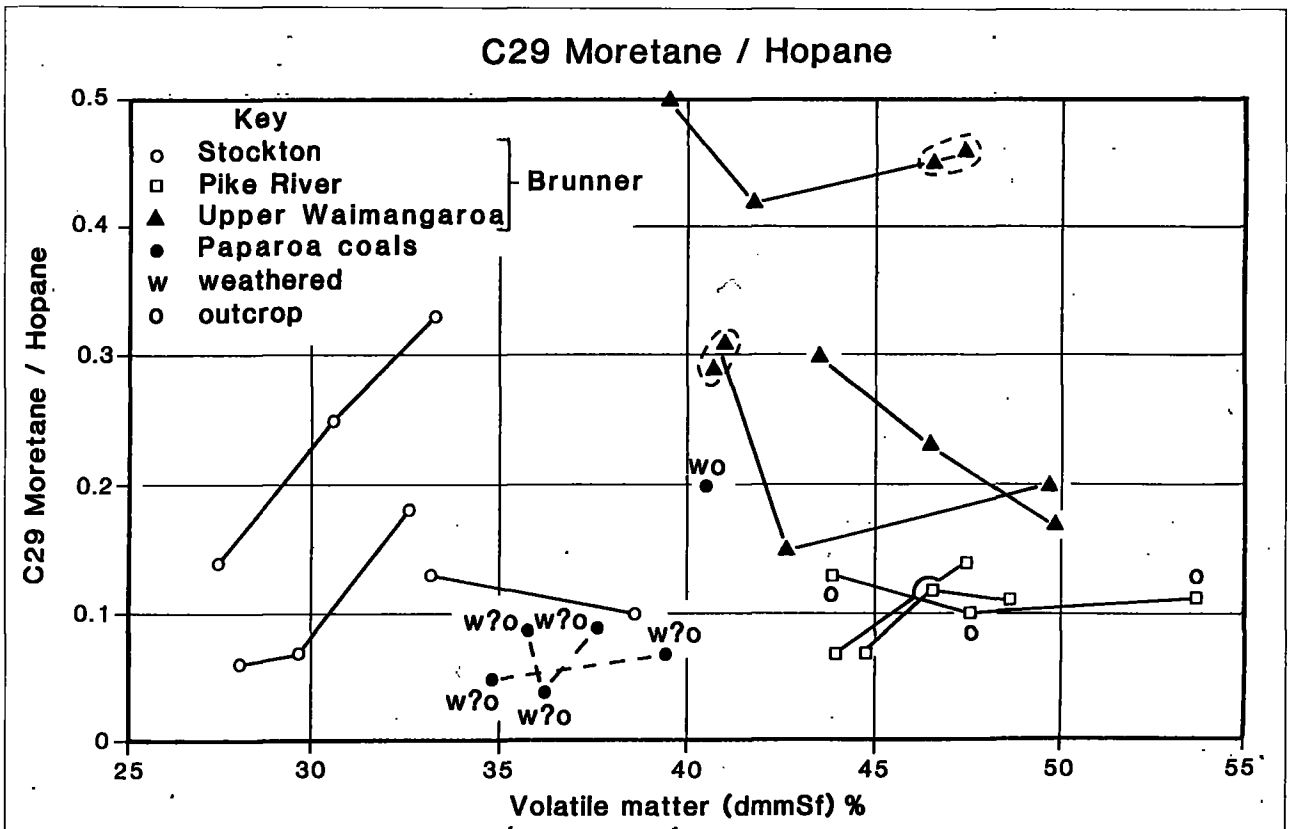


Figure 10: C29 moretane/hopane ratio values plotted against volatile matter.

C30 Moretane / Hopane

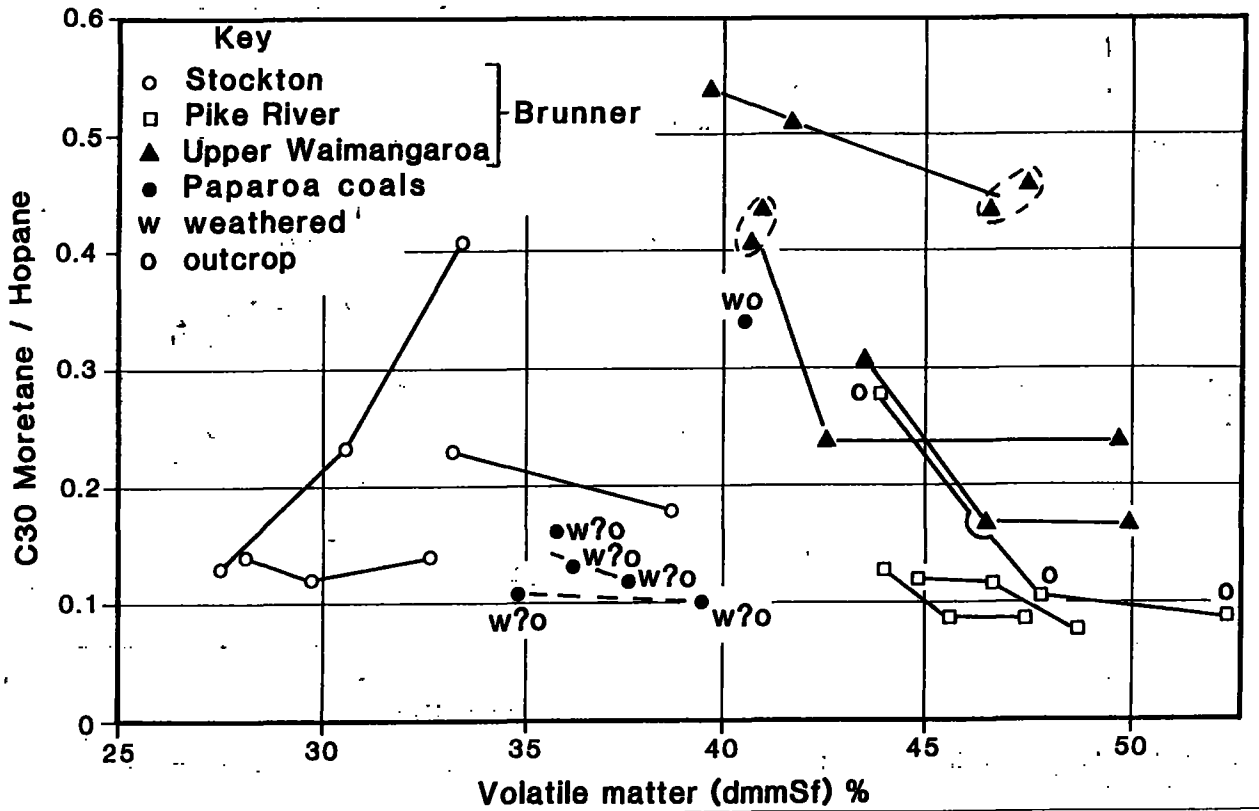


Figure 11: C30 moretane/hopane ratio values plotted against volatile matter.

C31 / C30 Hopanes

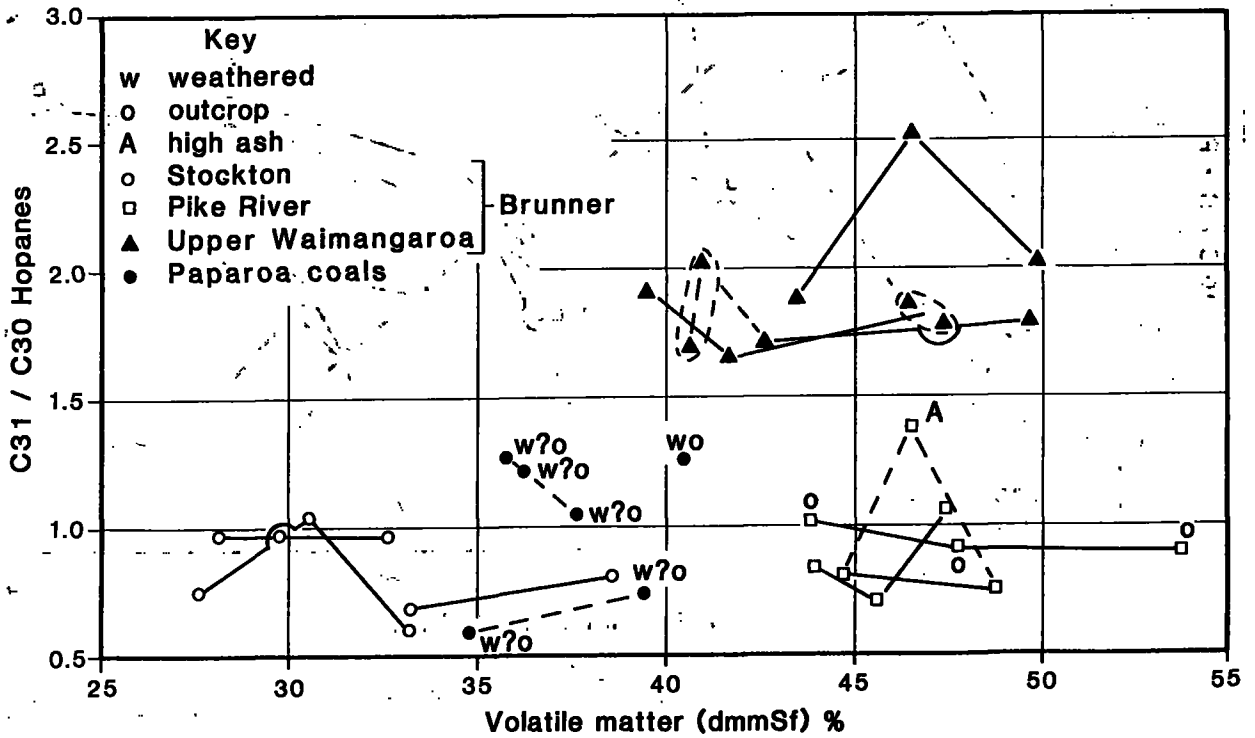


Figure 12: C31/C30 hopane ratio values plotted against volatile matter.

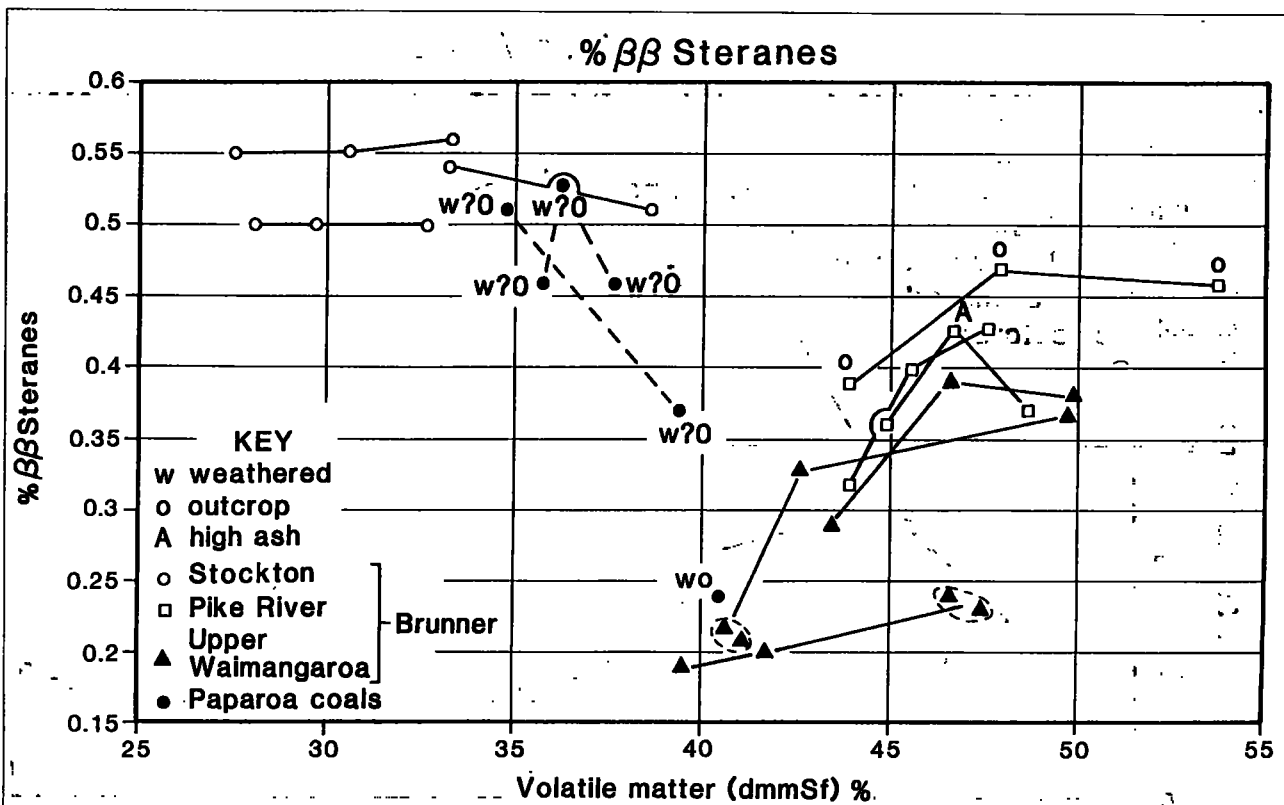


Figure 13: %ββ steranes plotted against volatile matter. Increasing values correspond to increasing maturity.

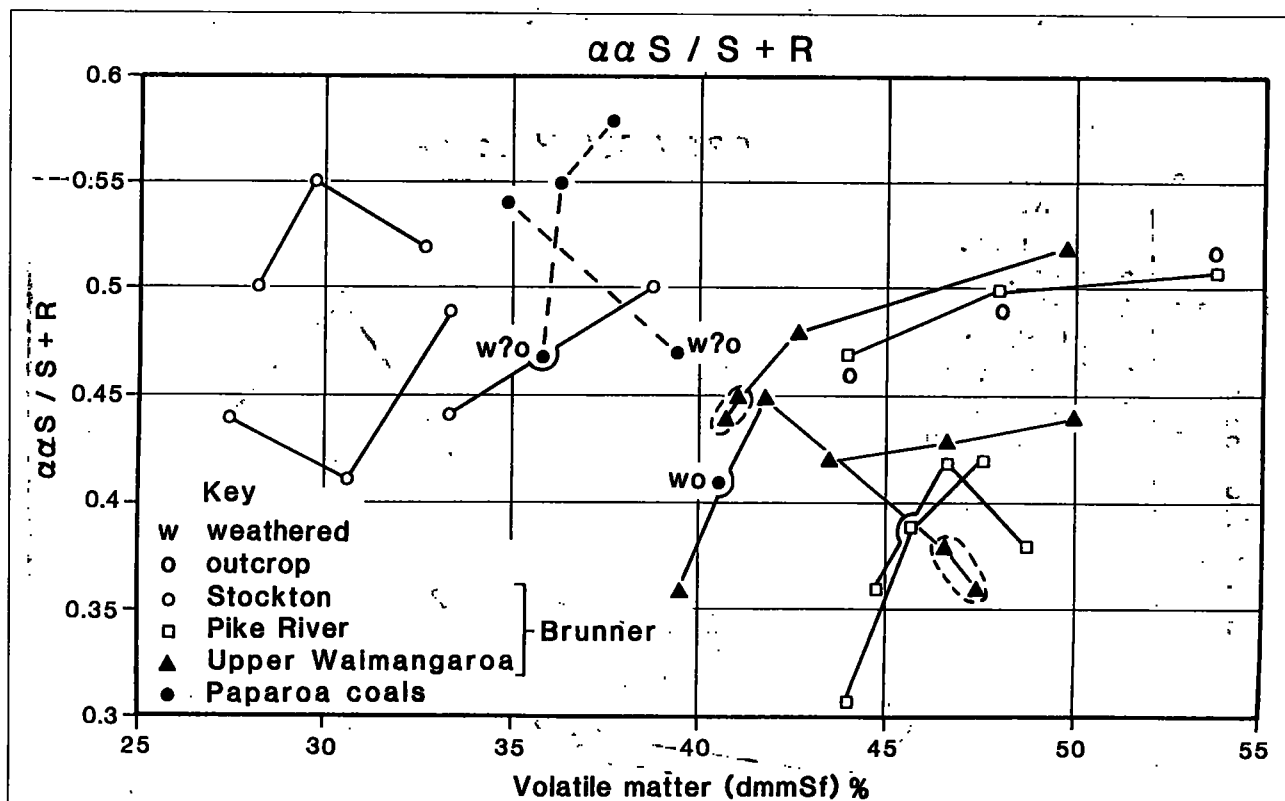


Figure 14: %ααS/S+R steranes, plotted against volatile matter. Conventionally, values increase with increasing maturity, but known relative coal ranks suggest that this biomarker ratio provides negligible maturity discrimination for the West Coast coal suite.

post-mature Stockton sample suites exhibit the opposite trend; highest volatile samples typically have similar or substantially *higher* biomarker ratio values. These trends together suggest that high volatile type coals may mature relatively early, and expel relatively early, in relation to temperature. The intermediate rank Paparoa samples are Cretaceous, and are from outcrops and old mine faces. They plot as mature except on the C29/C30 hopane plot, which appears very sensitive to partial expulsion. It appears likely that a mobile fraction has been lost due to weathering or biodegradation of these Paparoa samples.

Figures 15 and 16 show the graphical relationship between the C30 moretane/hopane and C31/C30 hopane biomarker ratios of the West Coast samples and published data for various Taranaki Basin coals and oils. It is apparent that Maui 4 oil, Kapuni-8 condensate, and the deepest Maui-4 coal, have biomarker values a little higher, (i.e., *less* mature) than minimum values for mature West Coast samples. This discrepancy seems to conflict with previous suggestions that it is the oil fraction itself, and not the remaining "host" coal, which confers a high maturity signature (low ratio value) on the C30 moretane/hopane ratio. However, there is no real anomaly, because biomarker ratio values for condensate and oil in the Maui Field are equivalent to minimum values for mature West Coast coal samples.

The sequence of events suggested above is summarised diagrammatically in Figure 17. The concept that some vitrinites may mature more rapidly than others is consistent with suggestions that vitrinites with high volatile characteristics result from inclusion of lipids. In addition, a common feature of high volatile type coals is elevated sulphur, principally organically bound and introduced from marine groundwater during early burial (Newman, 1991). The possible role of sulphur-bearing compounds as a direct influence on maturation rates may require consideration.

Most high volatile type coals in mature New Zealand sequences are Bortonian (middle Eocene) in age, but there are exceptions, and some Bortonian coals have *low* volatile matter type (Figure 5). West Coast coals of Bortonian age include much of the Brunner Coal Measures, and some Kapuni Group coals in the Taranaki Basin are also Bortonian and of a high volatile type. Therefore, the possibly distinctive maturation rates and source potential of Bortonian coals are relevant to both the Westland and Taranaki basins, although in the latter case mature Bortonian coals may not yet have been intersected by drillholes. Czochanska *et al.* (1987) document anomalous maturity values downhole in the Card Creek well south of Greymouth (Figure 18). Coals above a presumed Brunner/Paparoa contact were nearer to achieving maturity, based on biomarker ratios, than coals beneath,

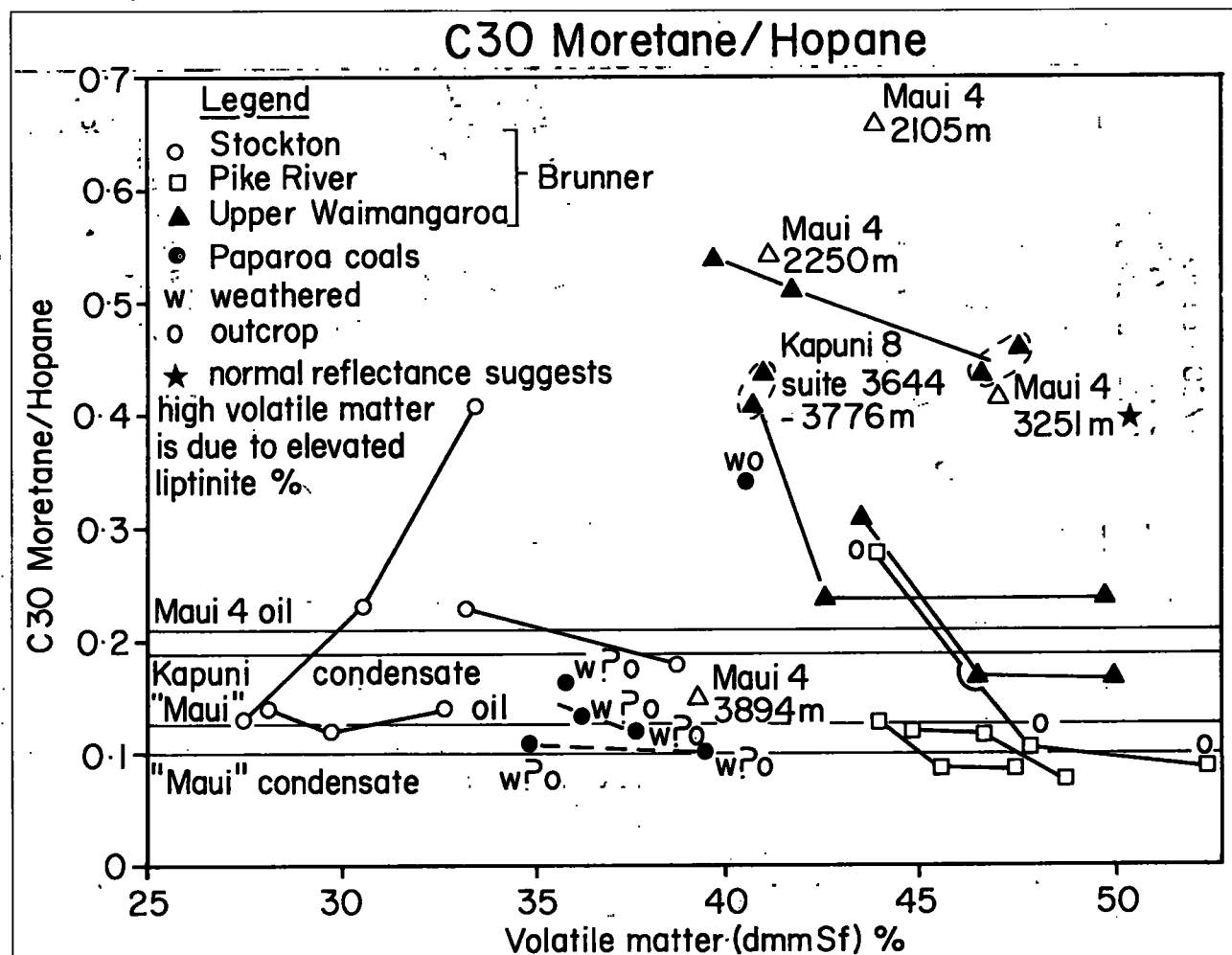


Figure 15. C30 moretane/hopane biomarker ratio values (from Figure 11) are shown in relation to values for Taranaki coals and oils. Values for high rank West Coast samples regress away from the oil compositions, possibly indicating separating of coal from oil during expulsion.

C31/C30 Hopanes

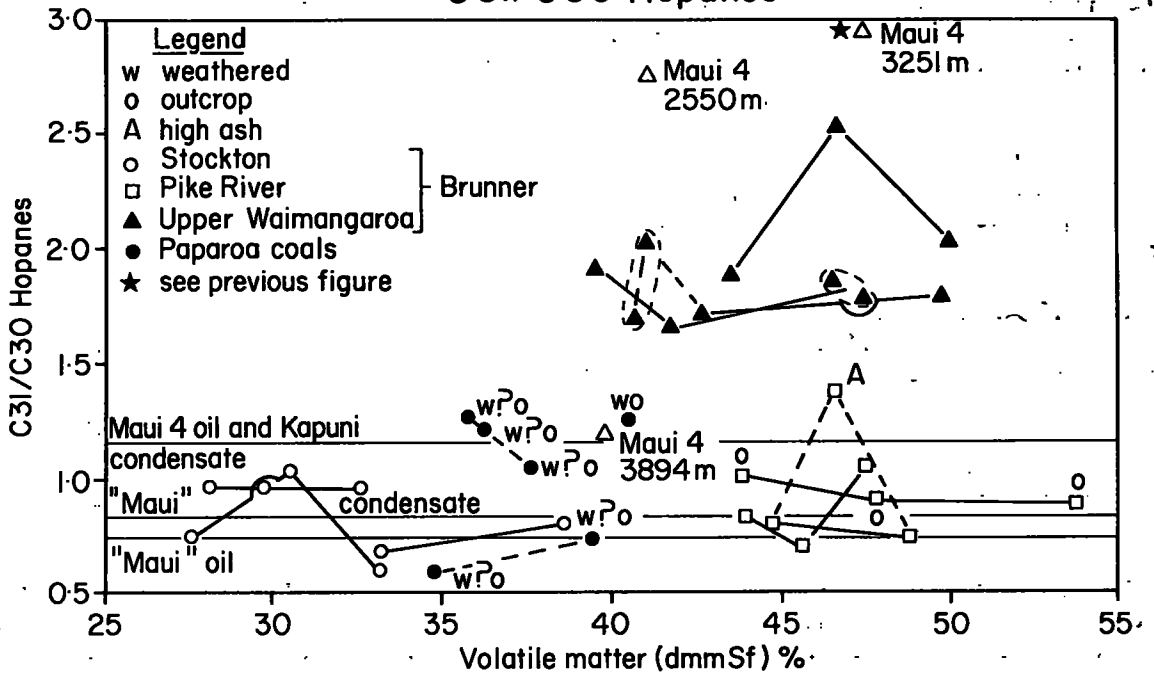


Figure 16: C31/C30 hopane biomarker ratio values (from Figure 12) are shown in relation to values for Taranaki coals and oils.

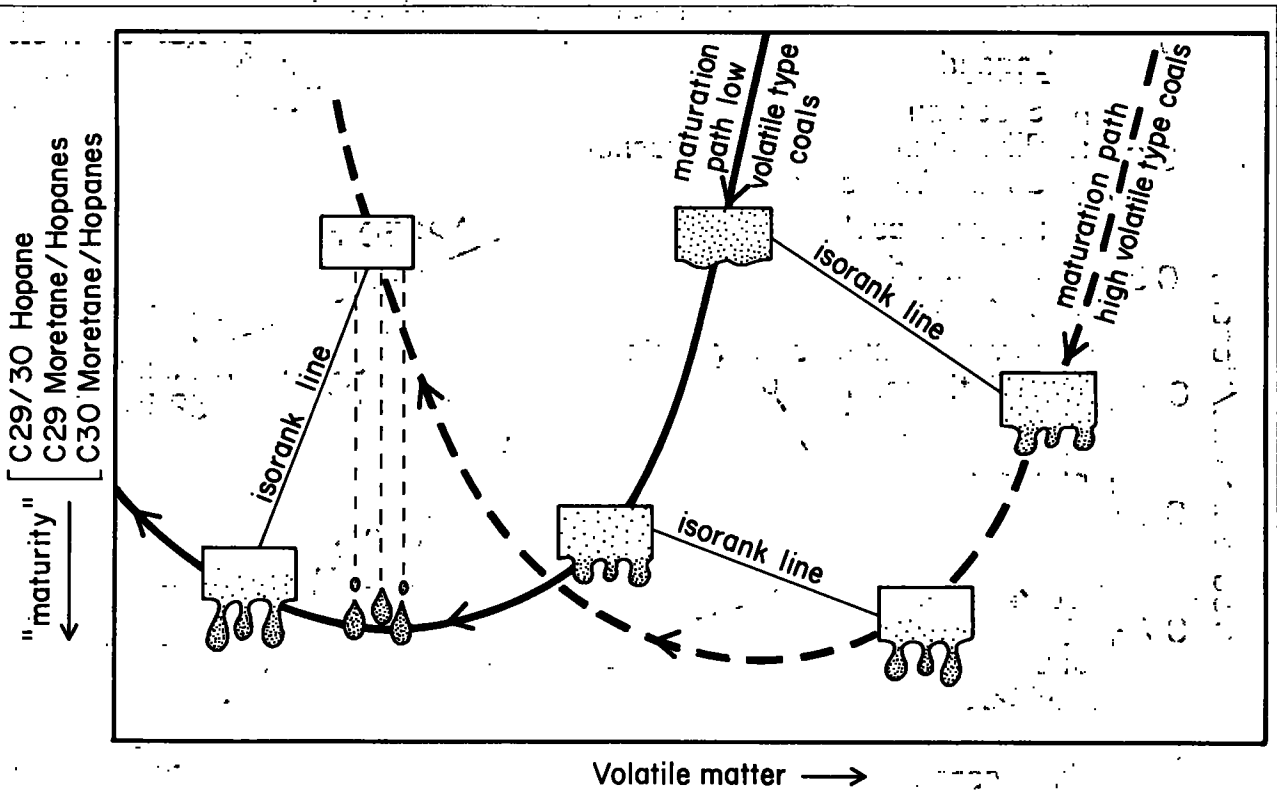


Figure 17: A schematic model illustrating a hypothetical explanation for the complex rank and type relationships of several hopane biomarker ratios (C29/C30 hopane, C29 moretane/hopane, C30 moretane/hopane). Observed trends indicate that perhydrous vitrinites may be generating and expelling oil relatively early in comparison to "normal" vitrinites. Serial samples of contrasting type are essential for demonstration of possible type effects.

although neither were mature. The C30 moretane/hopane values and degree of variation within the Card Creek group of samples was equivalent to that demonstrated by the Brunner seam in Upper Waimangaroa Drillhole 1281 (35/763-766).

Conclusion

Systematic analysis and interpretation of New Zealand coals can elicit much information of relevance to petroleum exploration. Placing specific samples in the context of type and rank ranges for all New Zealand coals allows precise application of vitrinite reflectance and bulk chemical data, as opposed to approximations which homogenise a database and ignore the potentially important information which can be obtained from the aberrations of individual samples. Serial sample suites provide the opportunity to evaluate the degree to which depositional controls on humic coals influence petroleum generation potential. The assumption that all Cenozoic coals have the same generation potential given a particular thermal history is in conflict with evidence from GCMS biomarker values, which imply that although maturation is strongly influenced by thermal history, it is also modulated by vitrinite chemistry, which can be widely variable. These issues can be partly avoided in the case of currently available Taranaki samples, many of which tend to approach "average-type" compositions. However other coals, of high volatile type, have been identified in both Taranaki and the Westland Basins, and have relevance to evaluation of source areas in which Eocene coals may have attained maturity.

Biomarker data for the West Coast samples pose questions which set the scene for continuing research. In particular, is the reversal in trend of some hopane ratios at high rank a consequence of expulsion, as postulated above? Why are so many biomarker ratio values dependant on type, as defined by volatile matter? For example, does their response to type

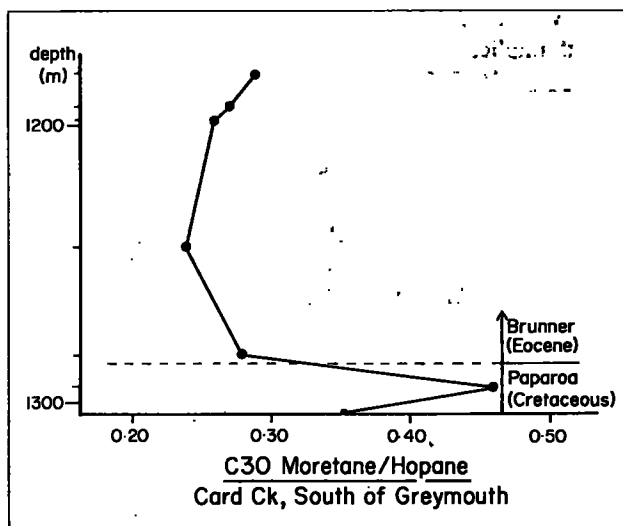


Figure 18: C30 moretane/hopane data for Cretaceous and Eocene coals in the Card Creek well, near Greymouth (reported by Czochanska *et al.*, 1988). Conventionally, declining ratio values correspond to increasing maturity. Reversal of the expected downward increase in maturation is attributed to contrasting vitrinite chemistry between some Eocene and Cretaceous samples.

variation really indicate that some coal types mature faster than others, in relation to temperature? Rock eval data are now available for the West Coast sample suite, and may help to answer some of these questions. Analysis of additional samples is also necessary to confirm observed trends and put a wider range of potential source coals into context. Results to date pose more questions than they answer, but one thing is clear; we don't yet know enough about some of the coals from which our petroleum may have been sourced.

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