

# THE STABLE ISOTOPE COMPOSITION OF SOME EAST COAST NATURAL GASES

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## Abstract

The carbon and hydrogen isotopic ratios of methane from 17 natural gas seeps on the East Coast of the North Island, New Zealand, show a diversity of values. All isotopic ratios are consistent with overseas values for gases associated with oil. Chemical compositions and geological settings are used to make further interpretations, and to relate the gases to possible source rocks.

Isotopic compositions suggest that mature source rocks have produced the gases from Otopotehetehe, Waitangi, Tukituki, Wairakau, Weber, Te Hōe and Langdale. The Rotokautuku gas appears to have been altered by secondary processes such as oxidation. Some of the gases are associated with oil seeps. Waimata gas may be from a less mature source than the above. All these gases have methane  $\delta^{13}\text{C}$  values more positive than  $-45\%$  implying probable  $R_o$  values greater than 1% if the source matter is of marine origin.

Kaikopu and Te Pohue gas seeps have more negative  $\delta^{13}\text{C}$  values implying they have been buried and/or heated to a lesser degree than the other gases.

The warm springs at Te Puia also evolve a mature methane-rich gas with saline water. A warm spring in the greywacke ranges at Mangatainoka is suggestive of a reasonable degree of thermal maturity, but is nitrogen-rich and identical to other springs on the same fault. Morere warm springs and nearby seeps and mud volcanoes at Kopuawhara and Tiromoana suggest variable mixtures of thermogenic gas with a microbial gas although their  $^3\text{He}/^4\text{He}$  values suggest a deeper gas contribution.

## Introduction

There are a considerable number of places in New Zealand where gases seep naturally from the ground. Many have been reported from both well-known and obscure localities by McLernon (1978) and some analyses were recorded by Ross (1967), but for many, modern analyses have not been published. In the East Coast of the North Island of New Zealand, many gas seeps, some associated with oil, have been reported. Many of these have been mapped by, or for, oil exploration companies.

To the east of the North Island of New Zealand, the Pacific plate is being subducted under the East Coast, resulting in complex geology, well described by others in this symposium (Francis 1991, Cutten 1991). To the south of Hawke Bay the area is dominated by northeast trending folds and faults reflecting the compressional tectonics, and to the north in the Gisborne area, there is a NNW-SSE trend as well. Around Hawke Bay itself, structural trends are masked by Pliocene and Quaternary rocks. The Triassic-Lower Cretaceous rocks of the Torlesse greywackes occur to the west of the East Coast Cretaceous to Quaternary basin and across a series of bounding faults. Fig. 1 summarizes the geology and shows the sample locations.

The East Coast gases are widespread from near East Cape in the north to near Masterton in the south, and the distribution of hydrocarbon-containing gas seeps closely

parallels the distribution of Cretaceous to Lower Miocene formations likely to be their source. Many gas seeps exhibit strong structural control, and are located on or near structural highs or major faults. However, others are related instead to permeable formations breached by surface erosion.

This present compilation looks in detail at the stable isotope composition (i.e. Deuterium/Hydrogen and  $^{13}\text{C}/^{12}\text{C}$ ) of gases from the East Coast, and incorporates additional new analyses to those reported in Lyon (1989). The East Coast gases are quite different from the mostly warm springs of Northland and West Waikato that were discussed at the 1989 New Zealand Oil Exploration Conference (Lyon 1990). There are only three areas of warm springs on the East Coast, at Te Puia, Morere and Mangatainoka. Other gases are cool or cold, and all have potential as indicators of oil or gas resources below them.

This study concentrates on the carbon-13 ( $^{13}\text{C}$ ) to carbon-12 ( $^{12}\text{C}$ ) ratio, and deuterium (D or  $^2\text{H}$ ) to hydrogen (H) ratio. These isotopes are all stable, and do not decay with time as do the rare heavier, unstable isotopes of carbon,  $^{14}\text{C}$  and hydrogen,  $^3\text{H}$  (tritium). The carbon-13 and deuterium concentrations are measured using sensitive mass spectrometers, and their concentrations (or ratios relative to the more common isotope) are reported as deviations from internationally recognised standards as  $\delta^{13}\text{C}$  and  $\delta\text{D}$  values, in parts per thousand (‰)

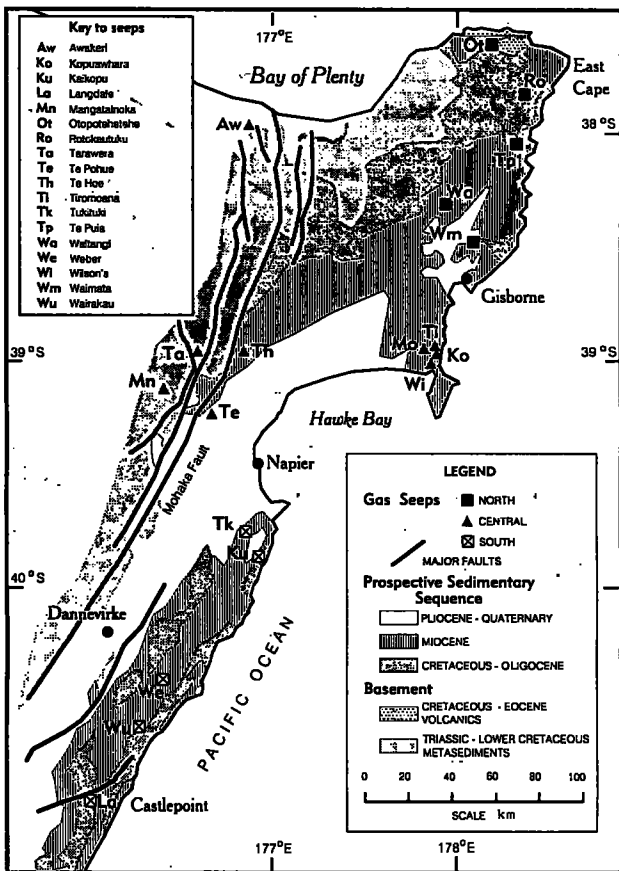


Figure 1: The East Coast region of the North Island, New Zealand, showing simplified geology (after NZGS 1972 and Moore *et al.* 1989) and the sample locations.

$$\text{i.e. } \delta^{13}\text{C}(\text{‰}) = 1000[(^{13}\text{C}/^{12}\text{C})_{\text{sample}} / (^{13}\text{C}/^{12}\text{C})_{\text{PDB}} - 1]$$

$$\text{and } \delta\text{D}(\text{‰}) = 1000[(\text{D}/\text{H})_{\text{sample}} / (\text{D}/\text{H})_{\text{SMOW}} - 1]$$

where PDB and SMOW are the international standards Pee Dee Belemnite, a fossil carbonate shell, and Standard Mean Ocean Water.

Recent reviews of the stable isotope data from many overseas natural gases (Schoell 1980, 1983, 1988) have given some guidelines for the interpretation of the isotopic compositions of methane-rich gases. Schoell (1983) has presented a detailed summary of the geochemistry and isotopic composition of natural gases, and related the analysed data to the genesis of the gases. Only a brief summary of those findings will be given in this paper. The characterisation is based on the data listed in Schoell (1980) of which most are from the USA and Europe, with 2 gases each from Egypt and the Philippines. However, Smith *et al.* (1985) have found, for Australian gases, that these Northern Hemisphere classifications are not necessarily applicable in the Southern Hemisphere.

Methane is formed from organic matter in a variety of environments. Wet gas (i.e. accompanied by higher hydrocarbons: ethane, propane, butane, etc.) forms during thermal reaction of buried organic matter at temperatures between 50 and 150°C and usually has methane  $\delta^{13}\text{C}$  values between 30 and 55‰ (Figure 2). Dry gas, with small or negligible amounts of ethane, can form during microbial anaerobic diagenesis at temperatures less than 70°C. If

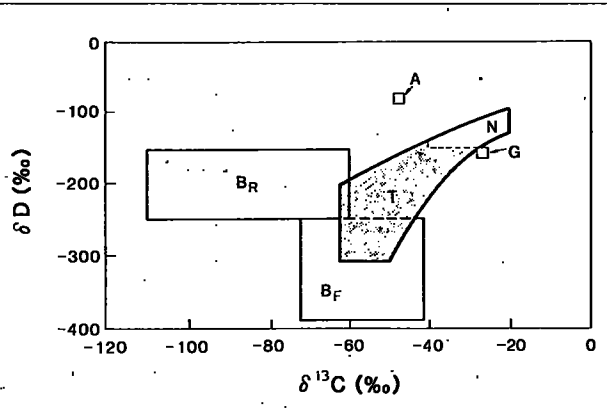


Figure 2: Deuterium and carbon-13 values for naturally occurring methanes (from Schoell, 1988). A = atmospheric methane,  $B_R$  = microbial gases produced from reduction of carbon dioxide,  $B_F$  = microbial gases derived from fermentation processes. G = most New Zealand geothermal gases (from Lyon and Hulston, 1984). N = thermogenic gases not associated with oils, T = thermogenic gases associated with oils and condensates.

reduction of carbon dioxide occurs then carbon isotopic fractionation is greatest and the methane is very depleted in  $^{13}\text{C}$ , i.e.  $\delta^{13}\text{C}$  values less than about -55‰. Under some situations, acetate fermentation occurs preferentially (Schoell 1988). Dry gas is also produced during thermogenesis after the higher hydrocarbons have already been formed, and removed, when higher temperatures may produce methane with  $\delta^{13}\text{C}$  values between -40 and -20‰. With increasing maturity (i.e. temperature), wetness decreases and also the heavy isotope content of the methane decreases. Thus overmature, dry thermogenic methane is relatively enriched in deuterium and carbon-13.

Although the methane  $\delta^{13}\text{C}$  value can depend on the type of source material also, Schoell (1983) attempted to relate the vitrinite reflectance  $R_o$  (a conventional measure of maturity) to methane with the equation.

$$\delta^{13}\text{C}(\text{CH}_4) = 17 \log R_o - 42$$

Although this must be used cautiously, it can be an indicator, i.e. that  $\delta^{13}\text{C}(\text{CH}_4)$  values more positive than -42 may imply source maturity with  $R_o > 1.0\%$ .

However, secondary effects also affect the isotopic composition of methane, and also the degree of wetness. In particular migration may fractionate the isotopes (Schoell, 1988) or may involve mixing of two or more different gases. Occasionally methane oxidation is observed, and this process enriches the residual methane in  $^{13}\text{C}$ , and also in D (Coleman *et al.* 1981, Whiticar & Faber 1986).

An additional indicator of maturity and gas type is the amount of higher hydrocarbons present. Schoell (1983) uses the term  $C_{2+}$  which is

$$C_{2+} = (1 - C_1 / \sum C_n) \times 100$$

where  $C_n$  is the content of molecular species with n carbon atoms, for n = 1 to 5.  $C_1$  is the content of methane. As discussed above, low  $C_{2+}$  values occur at immature and overmature stages of oil/gas generation. Migration has been reported to preferentially remove higher hydrocarbons, (Schoell, 1983) i.e. to reduce the  $C_{2+}$ , with little or no effect on the isotopic composition of the methane. A detailed study of Japanese natural gases by Igari and Sakata (1988) has shown that natural gases tend to lose their  $C_2$ - $C_4$  hydrocarbons



Site	Sampling date	Name	Temp. °C	Grid Ref. NZMS 260	Sample R No.	Flask BN
Ot	17 June 79	Otopotehetehe		Y14/637856	9026/2	17
Ot	26 Jan 84	Otopotehetehe	22	Y14/637856	11106/33	96
Ro	26 Jan 84	Rotokautuku	16	Z15/767571	11106/34	89
Tp	18 Jan 78	Te Puia	67	Z16/748359	5869/2	62
Tp	08 Aug 79	Te Puia	66	Z16/748359	5951/29	27
Tp	05 Dec 87	Te Puia	63	Z16/748359	11642/9	102
Wa	17 Jun 79	Waitangi oil		Y17/382061	9026/26	102
Wa	26 Jan 84	Waitangi oil		Y17/382061	11106/35	30
Wm	17 Jun 79	Waimata		Y17/507893	9026/27	104
Wm	03 Jan 88	Waimata	16	Y17/507893	11642/8	154
Central						
Mo	14 Feb 76	Morere	46	X19/256354	5137/1	
Mo	17 Oct 78	Morere, top	47	X19/256354	5775/1	25
Mo	17 Oct 78	Morere No 2	49	X19/256354	5775/2	26
Mo	18 Jan 79	Morere tank	49	X19/256354	5775/3	8
Mo	01 Jan 86	Morere No 2		X19/256354	11545/5	9
Mo	01 Jan 86	Morere 2 tank		X19/256354	11545/6	25
Ti	20 Jun 79	Tiromoana		X19/293354	9026/4	105
Ko	02 Jan 86	Kopuawhara	21	X19/293295	11545/7	55
Wi	15 Nov 77	Wilson's Farm		X19/284292	5649	BB
Th	July 90	Te Hoe		V19/412366	14015/5	82
Mn	14 Jan 87	Mangatainoka	51	U19/034212	11414/7	73
Te	20 Dec 90	Te Pohue		V20/259066	14049/14	116
South						
Tk	K & P (90)	Tukituki		V22/376513		
Tk	24 Mar 89	Tukituki	16	V22/376513	11781/1	114
Ku	K & P (90)	Kaikopu		V22/478429		
Ku	24 Mar 89	Kaikopu	18	V22/478429	11781/2	151
We	Sep 90	Weber		U24/985802	14049/13	70
Wu	03 Jan 86	Wairakau	21	U25/863588	11545/8	1
La	09 Oct 59	Langdale	15	T26/636267	608/2	
La	06 Nov 80	Langdale	21	T26/636267	9187/1	1
La	06 Nov 80	Langdale	21	T26/636267	9187/2	94
La	15 Jan 87	Langdale	17	T26/636267	11414/8	65

K & P (90) refers to data from Kvenvolden and Pettinga (1990).

Table 1: List of sample details.

collected, the most air-free sample data is plotted. Air and air-saturated groundwater have negligible helium whereas on this plot (Giggenbach & Goguel 1989), additional helium derived from crustal outgassing and uranium decay is indicated in all samples.  $N_2/Ar$  ratios vary due to possible air contamination in sampling, but also due to addition of  $N_2$  from organic material decay, or of  $^{40}Ar$  from radioactive decay of potassium.

The stable isotope data are shown plotted in Figure 4 overlying the empirical classification of Schoell (1988) with the addition of the zone of most New Zealand geothermal gases from Lyon & Hulston (1984). All samples from the East Coast are shown to have  $\delta^{13}C(CH_4)$  values which are depleted (more negative) relative to geothermal methane and enriched (more positive) relative to microbial gases. The triangle indicates the location of all Taranaki gases analysed by Lyon (1989) (cf. Figure 3). The higher hydrocarbons ( $C_2$  to  $C_6$ ) have also been analysed for the most

recent samples and for some Taranaki gases (Giggenbach, unpublished). Figure 6 shows the relationship between  $\delta^{13}C(CH_4)$  and  $C_{2+}$ . The maximum value of about 11% contrasts with Taranaki gases where values up to 31% have been recorded. The highest value here is for Waitangi oil seep where the gas is associated with oil. The diagram (Figure 6) conforms to the generalisation in Schoell (1983) where lightest  $\delta^{13}C(CH_4)$  values have low or negligible  $C_{2+}$ .

The relationships between some of the higher hydrocarbons (the alkanes  $C_2-C_6$ ) are shown for one sample from each site in Figure 7 with data for a McKee well (which had  $C_{2+} = 13.4\%$ ) shown for comparison. This McKee sample has a pattern very similar to the Taranaki gases from Maui and Kapuni. In this plot, migration as reported by Igarí and Sakata (1988) would tend to make three changes: move the line downward, straighten the line and steepen the line joining the concentration ratios of higher hydrocarbons.

Site	Sampling date	Name	Major components				<sup>13</sup> C <sub>PDB</sub> (K)		D <sub>SMOW</sub> (K)	<sup>3</sup> He/ <sup>4</sup> He x R <sub>Air</sub>
			CO <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	C <sub>2+</sub> %	CO <sub>2</sub>	CH <sub>4</sub>	CH <sub>4</sub>	
North										
Ot	17 June 79	Otopotehetehe	97	11	888	.05		-34.0	-155	
Ot	26 Jan 84	Otopotehetehe	41	22	934				-34.4	-138
Ro	26 Jan 84	Rotokautuku	19	7	973	3.2		-36.3	-116	0.3
Tp	18 Jan 78	Te Puia	6	90	844	3.3	-17.3	-40.6	-144	
Tp	08 Aug 79	Te Puia	191	13	772	2.2	-6.7	-42.0	-146	
Tp	05 Dec 87	Te Puia	87	33	877				-41.5	-143
Wa	17 Jun 79	Waitangi oil	89	33	867	9.8	-12.7	-35.8	-159	
Wa	26 Jan 84	Waitangi oil	0	27	970	10.9		-35.4	-151	0.08
Wm	17 Jun 79	Waimata	87	12	897	0.02		-40.8	-179	
Wm	03 Jan 88	Waimata	5	49	936	0.81		-41.5	-173	
Central										
Mo	14 Feb 76	Morere	23	15	950		-49.2	-161		
Mo	17 Oct 78	Morere, top	142	12	830	0.21	-12.8	-53.3	-179	
Mo	17 Oct 78	Morere No 2	50	12	927		0.21	-16.2	-53.4	-174
Mo	18 Jan 79	Morere tank	23	15	950		0.21	-14.0	-53.3	-176
Mo	01 Jan 86	Morere No 2	3	18	978		0.21		-53.0	-176
Mo	01 Jan 86	Morere 2 tank	3	20	975		0.24		-53.4	-176
Ti	20 Jun 79	Tiromoana	70	42	882		0.06	-14.9	-48.9	-183
Ko	02 Jan 86	Kopuawhara	8	52	940		0.1		-57.2	-177
Wi	15 Nov 77	Wilson's Farm	3	47	949				-49.4	-178
Th	July 90	Te Hoe		11	897		0.01		-38.8	-152
Mn	14 Jan 87	Mangatainoka		230	445		0.02		-37.3	-160
Te	20 Dec 90	Te Pohue	15	41	960		0.02		-50.7	-162

Table 2: Chemical and stable isotope analysis.

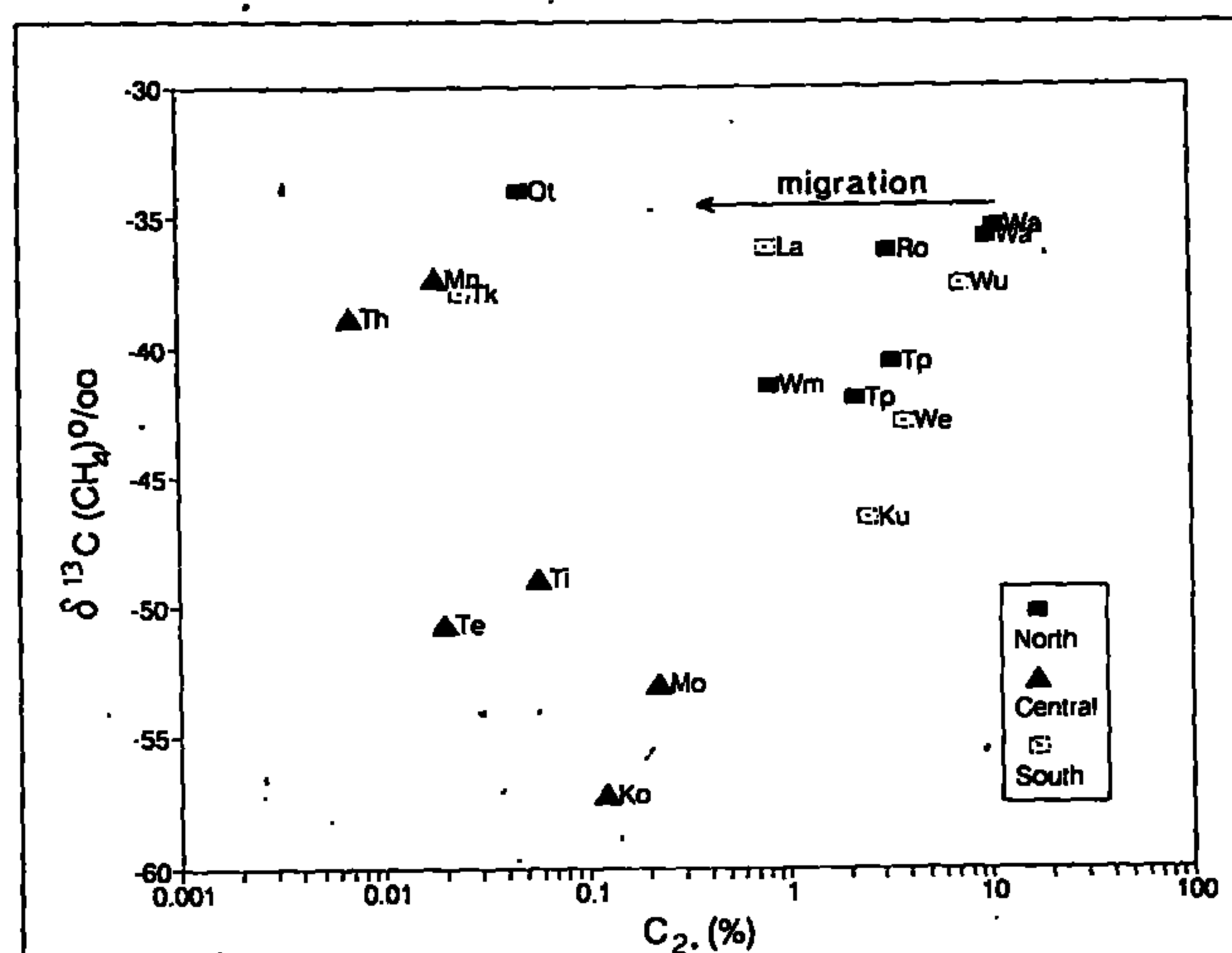


Figure 6: Higher hydrocarbon content relationship with <sup>13</sup>C. Symbols as for Fig. 1.

### Otopotehetehe

The seeps occur in an area of about 100 m by 25 m dotted with small mud volcanoes emitting brine and gas, and at times being explosively active. No oil has ever been seen in association with the gas seeps (McLernon 1978).

Bedrock in the immediate area is the Lower Tertiary Mangatu Group, but this is faulted against Cretaceous to Eocene Matakaoa Volcanics to the east, faulted against Cretaceous sedimentary rocks to the south, and overlain to

the west by Upper Miocene to Pliocene strata overthrust from the north.

The methane from this most northern site on the East Coast is the most enriched in <sup>13</sup>C implying that it is derived from sediments of greater maturity than are other East Coast gases. This gas has high helium content as shown on Figure 5, but its helium isotope ratio is identical to that of air and therefore mantle <sup>3</sup>He must be added in significant amounts (Sano *et al.* 1987) as well as <sup>4</sup>He. Figure 7 shows its very low higher hydrocarbon content consistent with it being overmature.

### Rotokautuku

The gas accompanies water and oil escaping from the shaft of the 200 m deep Rotokautuku well (McLernon 1978, Francis *et al.* 1991). Bedrock in the area is of Upper Cretaceous to Paleocene age, and the well is close to the fault contact with Lower Miocene strata (Moore *et al.* 1989). Much of the pre-Miocene is pervasively fractured, and probable fracture porosity is indicated in logs from nearby, more recently drilled oil exploration wells (Duff 1990).

The oil at Rotokautuku is slightly immature, probably of mixed marine and terrestrial origin, and has not as yet been matched geochemically to a source (Johnston *et al.* 1991: this volume; Hirner & Lyon 1989; Hirner & Robinson 1989).

The Rotokautuku methane is unusually enriched, in both <sup>13</sup>C and D (Figure 4), suggesting that it has been altered. This composition is consistent with microbial oxidation which could occur in the old well shaft where oxygenated

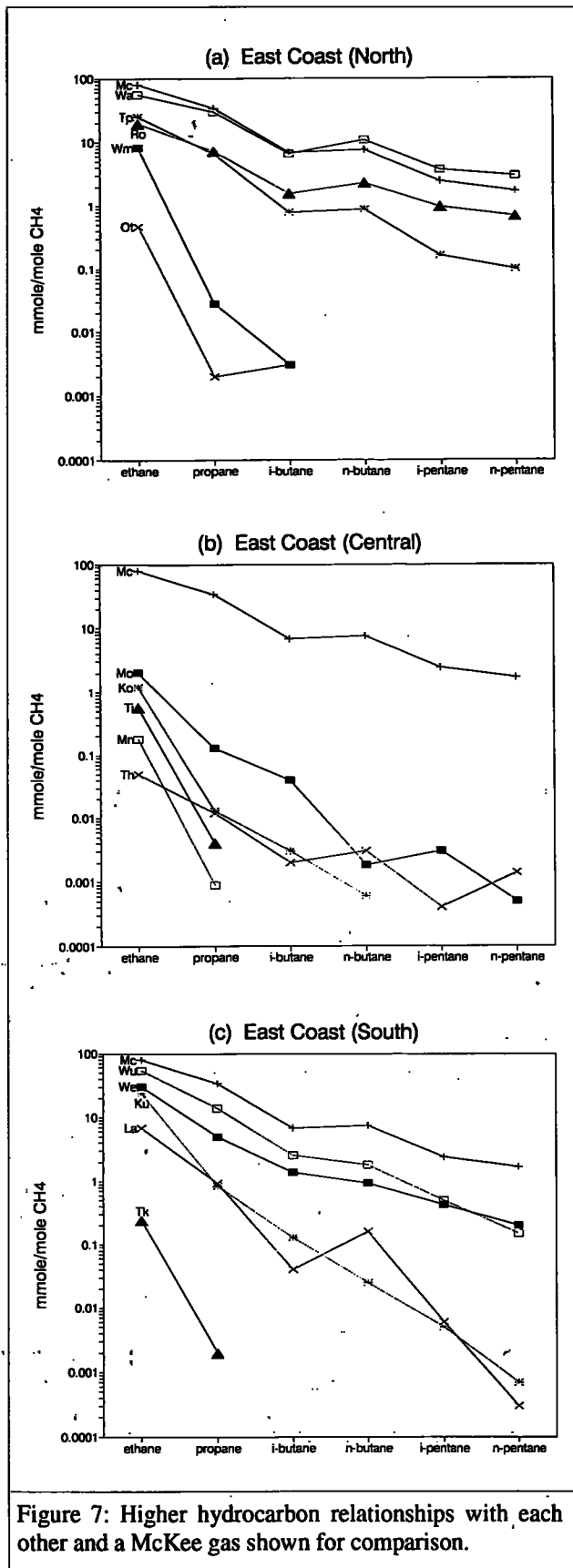


Figure 7: Higher hydrocarbon relationships with each other and a McKee gas shown for comparison.

groundwater could mix with the oil and gas. This would imply an original isotope composition which is at a slope of about 8 (Coleman *et al.* 1981), more negative toward a value of that for Te Puia or Kaikōpu (Brookby) depending on the proportion removed by oxidation. A composition near to that of Kaikōpu would be consistent with the slight immaturity

mentioned above. Probably less than 50% of the methane has been removed by this process. This gas is associated with oil and the higher hydrocarbon relationship (Figure 6) show similar patterns to the gases at McKee (Taranaki).

### Te Puia

In the immediate area of the hot springs and gas seeps, bedrock consists of Paleocene to Eocene Wanstead Formation (Francis *et al.* 1991). However, Te Puia is situated on a complex faulted dome exposing Cretaceous to Oligocene rocks in its core, and surrounded by generally radially dipping Lower to Upper Miocene strata. Although high in ethane content, the Te Puia gas is not directly associated with oil at the surface.

This hot spring area is only about 20 km south of Rotokautuku, and has temperatures up to 67°C. The methane stable isotope composition is in the range of thermogenic gases and the gas composition, being methane-rich is not consistent with volcanic heating. The hot spring water is saline and enriched in the heavy isotopes (Glover 1968, Allis & Stewart 1988) implying that it is of connate origin. It appears that tectonic forces are expelling the water and its associated gases from buried marine sediments at a depth of more than 2 km to account for this high temperature.

### Waitangi

At the Waitangi seeps, oil predominates over gas, which escapes in minor quantities with slightly warm brine. The Waitangi seeps are situated on a minor fault crossing an elongate NE-trending structural high. Within this high are tightly folded and pervasively faulted Upper Cretaceous to Oligocene rocks, with Lower to Mid-Miocene strata dipping to the southeast and northwest.

The oil in the Waitangi seeps is of predominantly terrestrial origin and slightly immature (Johnston *et al.* 1991) but with significantly more marine influence than Taranaki oils (Hirner & Lyon 1989; Hirner & Robinson 1989). As with Rotokautuku, it has not been matched geochemically to a source formation.

The gas from this oil seep is similar in isotopic composition to that from Otopotehetehe but has a very much higher ethane content and less carbon dioxide. The higher hydrocarbon pattern (Figure 7) is very similar to that from McKee in Taranaki.

### Waimata

Several gas seeps are associated with mud volcanoes in the Waimata area (Francis *et al.* 1991). Brine is produced in association with the gas. During and after strong earthquakes, the mud volcanoes have been recorded as increasing in activity, or erupting mud and boulders to a height of 120 m above ground level (Strong 1931).

The mud volcanoes associated with the seeps conceal much of the local geology, but they are situated on a faulted anticline exposing mid-Miocene rocks in its core, and surrounded by upper Miocene to Pliocene strata. Bentonitic mud is most likely derived from remobilised Wanstead Formation (Paleocene to Eocene) and erratic boulders thrown out of the volcanoes include rocks of definite Upper Cretaceous age.

The Waimata gas seeps are situated on the intersection of the NNE-trending Urutaranga Anticline and the east-west trending Whangara High. The Waimata seeps are separated

from the Waitangi oil and gas seeps 20 km to the NNW by the major Waihora Syncline and other structural complications. About 5 km stratigraphic thickness of Miocene and Pliocene marine sedimentary rocks occur in the Waihora Syncline, and also in the Waimata Syncline to the southeast.

Seeps occur on almost every structural high in the Gisborne region (Francis *et al.* 1991), and the most active of these are associated with mud and brine volcanoes.

The Waimata sample is probably from the Arakihi Road mudspring of McLernon (1968) and Ridd (1970). The isotopic composition (Figure 5) suggests a lower degree of maturity than the Waitangi gas but still within the normal oil-window range. However, it is very depleted in hydrocarbons larger than C<sub>2</sub> (Figure 7a) showing that migration has occurred.

#### **Morere, Kopuawhara, Wilson's Farm, Tiromoana**

Bedrock in the vicinity of all of these seeps is the Mid-Miocene Tunanui Sandstone, a thick-bedded formation with some reservoir potential. The Morere warm springs are situated on the Morere Anticline, which trends north to northeast. The Kopuawhara and Tiromoana gas seeps are situated on a north-trending fault which intersects the Morere anticline to the north. Paleocene to Oligocene rocks are exposed in a small horst adjacent to the Kopuawhara Fault, and the Kopuawhara and Tiromoana seeps are situated on small mud and brine volcanoes similar to that described for Waimata above. The Wilson's Farm seeps are located on the northern part of the Opoutama Anticline, which is an en echelon structure sub-parallel to the Morere Anticline. The Gisborne-1 well was drilled in 1927 on the Morere Anticline, and Morere-1 (1940) and Opoutama-1 (1967) were drilled on the Opoutama structure south of the Wilson's Farm seeps. All had minor gas shows. The structure in the area of these seeps is relatively gentle compared to that of the complex Waitangi, Te Puia, Rotokautuku, Whangara-Waimata, and Otopotehetehe areas.

This series of warm springs has saline, isotopically enriched water up to a temperature of 49° (Allis & Stewart 1988; Downes *et al.* 1980; Glover 1968; Nathan 1974). As at Te Puia, the gas is dominated by methane. Three gas analyses show identical isotopic compositions but the earliest isotopic analysis is distinctly different. The gas composition is at the more negative  $\delta^{13}\text{C}$  side of the thermogenic range of Schoell (1988) as shown in Figure 6. It is possible that the gas is a mixture of thermogenic gas with a microbial gas of  $\delta^{13}\text{C}$  value less than -60‰. The higher hydrocarbon contents are low (Figure 7b) and the ratios iso/normal for butanes and pentanes are greater than 1, in contrast to values  $\leq 1$  for Waitangi and Taranaki gases. This suggests that migration has significantly affected these gases, in the order Tiromoana > Kopuawhara > Morere.

The Kopuawhara, Wilson's Farm and Tiromoana samples all have very similar  $\delta\text{D}$  values and  $\delta^{13}\text{C}$  within  $\pm 5\%$  of Morere suggesting a geochemical relationship, possibly due to different proportions of a mixture of thermogenic and microbial methane. All the sites are in a circle about 10 km diameter (although the Tiromoana site is less precisely known). Those with highest CO<sub>2</sub> content have similar  $\delta^{13}\text{C}(\text{CO}_2)$ , about -15‰.

The two samples Kopuawhara and Morere that have been analysed for <sup>3</sup>He/<sup>4</sup>He show high values: 2.5 and 2.7

times the atmospheric ratio, respectively (Sano *et al.* 1987). These values are higher than any other values from the East Coast. These two similar values, and their similar water chemistries (Glover 1968) also suggest they are related. Giggenbach *et al.* (in preparation) suggest these high helium values may be explained by seepage of mantle gas up the decollement of the oceanic sediments on the downgoing Pacific Plate under the East Coast.

#### **Te Hoe**

The Te Hoe gas seep is associated with brine seeps, and is located on a major fault juxtaposing Lower Miocene and Upper Miocene. The fault trends NNE from the core of the Te Hoe Structure (Stoneley *et al.*, 1958). The seep is 4 km east of the major bounding Mohaka Fault, which juxtaposes the Cretaceous to Upper Miocene sequence against Triassic-Jurassic basement to the west. East of the seep, very thick (5 - 7 km) Miocene - Quaternary sedimentary sequences dip ESE into the Wairoa Syncline.

The Te Hoe-1 exploration well was drilled 3 km south of the Te Hoe seep in 1990. Shows of gas were reported on testing.

The isotopic composition of Te Hoe methane (Figure 5) from the gas seep indicates that it is derived from quite mature sediment, perhaps over-mature to explain the very low higher hydrocarbon composition (Figure 7).

#### **Mangatainoka (Puketitiri)**

These hot springs are by the Mohaka River in the Triassic-Jurassic Torlesse rocks of the Kaweka Ranges. They are located near a major fault zone (Figure 1) which has a series of hot springs throughout its length, northeast to Awakeri (Allis & Stewart 1988). Awakeri, in eastern Bay of Plenty has methane with an isotopic composition almost identical to that of Mangatainoka (Lyon 1989). The Mangatainoka spring waters are dilute, and similar in isotopic composition to meteoric water (unpublished data), but Awakeri, Mangatainoka and Tarawera hot springs are all similar with unusually high boron and fluorine contents (Glover 1968).

In contrast with all other gas seeps discussed here, there is no possibility that the Mangatainoka gas has been derived from the likely petroleum source rock sequence of the East Coast (Lower Cretaceous-Miocene). The only younger rocks exposed in the area are thin, isolated outliers of upper Miocene strata.

The chemical and isotopic indicators suggest that along the fault zone, meteoric water is circulating to similar depths and temperatures with methane being derived from sediments of the same composition and degree of maturation. The gas is nitrogen-rich but methane is significant and although it has the lowest CH<sub>4</sub>/N<sub>2</sub> (and CH<sub>4</sub>/Ar and CH<sub>4</sub>/He) ratio among these samples it does not have a high He/N<sub>2</sub> ratio (Figure 5) implying its helium accumulation time has been less than that of the other samples.

#### **Te Pohue**

Several seeps occur in the area, and these are associated with weak emanations of sulphur-smelling brine. Bedrock in the area is gently southeast-dipping upper Pliocene calcareous sandstone, and minor NNE-trending faults interrupt and locally repeat the sequence. Highly permeable Pliocene coquina limestone of the Te Aute Facies probably underlies the area of the seeps.

The thickness of the sedimentary sequence here is uncertain; Lower Pliocene directly overlies Triassic-Jurassic basement 5 km southwest of the seeps, at Opau Stream (Stoneley *et al.* 1958), but the more complete Cretaceous-Tertiary sequence of the southern Wairoa Syncline and Napier basin is certainly present down-dip to the east and southeast.

The isotopic data, and lack of measurable higher hydrocarbons larger than ethane suggest a microbial gas derived from shallow sediments.

#### **Tukituki (Campbell's), Kaikopu (Brookby Station)**

At Tukituki, a group of four seeps is located on or close to the axis of the Elsthorpe Anticline. Gas from the most productive seep is trapped in a miniature gasometer, and is the source of this analysis.

The Elsthorpe Anticline is cored by faulted, probably eastward-thrust, Upper Cretaceous to Oligocene rocks, and flanked by thick (2500 m +) mid-Miocene to Pliocene strata (Kingma 1971; Pettinga 1982; Kvenvolden & Pettinga 1989). Lower Miocene rocks are locally thin or absent on the Elsthorpe Anticline, although they are present 20 km to the south, and may be present at depth farther west in the deeper parts of the Patatanga Syncline. There is a regional unconformity in the Mid-Miocene, so that shallow-facies Mid-Miocene rocks overstep Upper Cretaceous to Lower Miocene.

The gas is probably derived from the west of the Elsthorpe Anticline, and is migrating to the surface up the moderate- to low-angle faults in its core.

The Kaikopu seep is located on the Coastal High, separated from the Elsthorpe Anticline to the west by the Atua Syncline. The Coastal High consists of tightly-folded and imbricated Upper Cretaceous to Lower Miocene rocks; thrust faults dip west (Pettinga 1982; Kvenvolden & Pettinga 1989). The sequence in the flanking Atua Syncline locally includes only Upper Miocene and Pliocene strata, which is significantly thinner than the Neogene in the Patatanga Syncline (Kingma 1971; Pettinga 1982).

The gas in the seep is most likely derived from the west of the coastal high, and is migrating up low-angle faults as with the Tukituki seeps.

The Tukituki gas has a much more enriched methane isotopic composition, lower ethane and other higher hydrocarbon content and higher relative helium content, than the Kaikopu gas. These are consistent with a much higher maturity (overmature?) of the Tukituki seep ascribed by Kvenvolden and Pettinga (1989) to the variation in Miocene cover thickness, and, also consistent with considerable migration effects.

#### **Weber (Franklin's)**

This single gas seep is located 200 m east of the Titree Anticline, a steep-limbed, gently north-plunging fold locally cored by Lower Miocene strata. The Titree Anticline is an en echelon fold situated between the Auster and McCartie Synclines. Both synclines and the anticline are within the larger NNE-trending Akitio Synclinorium ("Akitio Syncline") which is contiguous with the Patatanga Syncline to the north. The Miocene to Lower Pliocene sequence on the east limb of the Akitio Syncline is over 3000 m thick, even though there is a prominent erosion break and unconformity in the mid-Miocene (Francis 1990).

Lower Cretaceous to Eocene rocks are exposed in the Whangai High and the Owahanga Tectonic zone to the east and west of the Akitio Syncline, and are most likely to be present beneath the Miocene. Source rock sequences are present in Cretaceous and Paleocene, and have probably been buried to generation depths in the Akitio Syncline. Weak and strong oil impregnations and seeps are present in the area, and several other wet gas seeps are present, particularly on the east flank of the Akitio Syncline near the contact of basal Miocene on to Paleogene.

The methane from this site plots near the centre of Figure 5, within the range of Taranaki gases. It is a wet gas (Figures 6 and 7c) but depleted in the heavier components relative to Taranaki and Waitangi gases, and indicative of some migration.

#### **Wairakau (Glencoe, Humphrey's)**

This seep is located on the eastern flank of the Akitio Syncline, and issues directly from north-west-dipping thick-bedded Lower Miocene sandstone (reservoir characteristics unknown). The thickness of overlying Miocene strata probably exceeds 2500 m, and the basal Miocene nearby overlies complexly folded and faulted Upper Cretaceous to Oligocene rocks to the east. It is probable that source rock sequences of Paleocene and Cretaceous age probably extend under the thick Miocene.

The major Tinui Fault, 2 km southeast of the seep, juxtaposes the Lower Cretaceous basement complex in the core of the Owahanga Tectonic Zone. Several oil impregnations are known within 10 km of this seep; biomarker studies indicate a mature oil of mixed marine and terrestrial origin (Johnston *et al.*, 1991).

The Wairakau gas has a similar  $\delta^{13}\text{C}$  and slightly more enriched  $\delta\text{D}$  value than Tukituki implying a similar degree of maturity. However, the higher hydrocarbon content is high showing that it has not become overmature to the extent of having lost its higher hydrocarbons, although some migration effects are apparent (Figure 7c).

#### **Langdale**

The seep is located within 100 m of the Adams Fault, which separates Lower Cretaceous Mangapokia and Taipo formations from Upper Cretaceous to Eocene Whangai, Waipawa, and Wanstead formations (Moore & Speden 1984). Although there is at present no Neogene cover, remnants in the Whareama Syncline, 2.5 km + to the east indicate an original burial by at least 2 km of Miocene strata.

Other nearby seeps include the Blairlogie, Mangapakeha, and Ica gas seeps, most of which contain significant amounts of ethane and higher hydrocarbons (Johnston 1980). Oil impregnations are known from Lower Cretaceous rocks 3-4 km west of the seep. Biomarker studies indicate a mature oil of mixed marine and terrestrial origin (Johnston *et al.* 1991).

Analyses dating back to 1959 show very similar  $\delta^{13}\text{C}$  values for the Langdale seep (Hulston & McCabe 1962a, 1962b). The gas is isotopically more enriched than any other of the gases south of Hawke Bay suggesting a greater degree of maturity of its source sediments. It does contain significant ethane, although lower levels than found in Weber and Wairakau gases (Figure 7) implying significant migration. However the Langdale gas also has a high relative helium content implying a long He-accumulation.

## Conclusions

The East Coast methane-rich gases show a range of carbon and hydrogen isotopic compositions which are all in, or close to, the range for thermogenic gases as identified empirically by Schoell (1988). The gases from the southern region (Weber, Wairakau, Langdale) all indicate a reasonable

level of maturity, in general agreement with the gc/ms results from oil impregnations in the same area (Johnston *et al.* this volume). Additionally the maturity indicated by gas from Tukituki suggests that the mature zone extends at least as far north as the Napier region.

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