

THE ISOTOPIC AND CHEMICAL COMPOSITION OF NATURAL GASES FROM THE SOUTH ISLAND, NEW ZEALAND

G L Lyon and W F Giggenbach
Nuclear Sciences Group
Institute of Geological and Nuclear Sciences
PO Box 31 312, Lower Hutt, New Zealand

Abstract

Analyses of seep gases from the prospective petroleum areas of Marlborough, Westland and Southland and of gases associated with other warm and cold springs in the South Island are presented and compared with those from Taranaki and elsewhere.

Isotopic analyses of gases from the sedimentary basins show that CH_4 from southern Marlborough is derived from mature sources, that from Wharf Stream being the most mature of the South Island hydrocarbon-rich gases. Three gases from the Murchison Basin show increasing maturity from W to E, with isotopic values similar to those for the McKee field. Gases from Kotuku (Westland) appear to be derived from thermogenesis at low maturity levels. Gas from the Hindley Burn (Western Southland) is probably derived from a source similar to that of the gas collected from a well drilled into the Ohai coal deposit. Gases from three areas, Marlborough, the Murchison Basin and Kotuku, have high (>5%) ethane contents and high N_2/Ar ratios confirming formation from mature sources and their potential for hydrocarbon production.

Gas from an alluvial delta in Lake Te Anau is produced through microbial reduction of CO_2 from decomposition of buried vegetation. In contrast an unusual H_2 -rich gas from Fiordland contains CH_4 similar in C isotopic composition to gases from greywacke, but with very depleted H isotopic composition probably due to abiogenic reduction. Several warm spring gases from fault zones are CO_2 -rich or N_2 -rich and some have microbially oxidised, isotopically enriched CH_4 . CH_4 from Hanmer Springs and some of the other fault springs have thermogenic compositions resembling those of gases from greywackes of the axial ranges of the North Island.

Ratios of $^3\text{He}/^4\text{He}$ for most gases are generally above crustal values (>0.1 R_A) implying addition of mantle fluids. High values >2.5 R_A are observed in CH_4 -rich gases discharged in the Murchison and Grey Valley basins, in Fiordland (H_2 -rich) and in East Otago (CO_2 -rich).

Introduction

The tectonic environment of the South Island is determined by its position on an active plate boundary. To the north-east, the Pacific plate is being subducted under the East Coast of the North Island and extending south to the Marlborough area of the South Island. To the south-west, the Indian-Australian plate is being subducted under the South Island. Between these two zones of subduction, transcurrent faulting splits the South Island, and the resulting stresses and movements during the Tertiary period have allowed several sedimentary basins to develop. Although not as common as in the North Island, gases seep from the ground in many places in the South Island. A number of these seeps are described in the compilations of McLernon (1978) and Mongillo and Cleland (1984). Some of the gases have been sampled and analysed before (Ross, 1967), but for many, modern analyses are reported here for the first time.

This study builds on earlier surveys and uses recent data, in particular stable isotopic compositions, to characterise the gases and to provide a preliminary interpretation that is useful in the assessment of hydrocarbon resources. The work complements earlier papers on North Island gases (Lyon, 1990, Lyon et al., 1992).

Methods

Sample collection

Gas samples consisting predominantly of hydrocarbons were collected into 300 to 400 mL evacuated glass bottles (Giggenbach, 1975). For samples containing dominantly CO_2 , evacuated flasks containing about 50 mL of 4 M NaOH solution were used. Most springs or seeps were sampled by inverting a funnel over the gas seep at the bottom of its water pool source if possible, and conducting the gas to the flask through Ti and butyl rubber tubing. Some of the gases were collected by inverting a plastic or glass beverage bottle over a funnel-underwater, to be transferred later into evacuated glass bottles for analysis.

Sample analysis

Chemical and mass spectrometric analyses were carried out as described in Lyon & Hulston (1984). For gases with CH_4/H_2 ratios >200, oxidation of CH_4 was by reaction of the gas with CuO at 800°C; for H_2 -rich gases an earlier oxidation step over CuO at 300°C prepared H_2 for isotopic analysis. The use of a liquid N_2 -cooled trap prior to oxidation, ensured that CO_2 , water, ethane and higher hydrocarbons did not enter the oxidation system. Since 1984 all D/H analyses have been prepared by the "hot-shot" zinc method (Stanley et al., 1984).

The stable isotopic ratios $^{13}\text{C}/^{12}\text{C}$ and D/H are measured using specialised mass spectrometers and the ratios are determined and reported as deviations from internationally recognised standards as $\delta^{13}\text{C}$ and δD values in parts per thousand (‰).

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

$$\text{and } \delta\text{D} (\text{‰}) = 1000 \left[\frac{(\text{D}/\text{H})_{\text{sample}}}{(\text{D}/\text{H})_{\text{SMOW}}} - 1 \right] \quad (2)$$

where PDB and SMOW are the international standards Pee Dee Belemnite, a fossil carbonate shell, and Standard Mean Ocean Water. For CH_4 , analytical precision for $\delta^{13}\text{C}$ is about $\pm 0.2\text{‰}$, and for δD about $\pm 3\text{‰}$.

Results and Discussion

This study extends earlier surveys and provides recent results on the chemical and isotopic composition of a representative set of South Island gases. Sample locations are shown in figure 1 and listed in table 1. For the present evaluation, the discharges may be grouped, from north to south, into several discrete types. Methane-rich gases are produced from the Marlborough sedimentary sequence in the southern extension of the North Island's East Coast Basin, and the Murchison, Westland (Nathan et al., 1986) and Southland (Turnbull et al., 1993) basins. Along the Alpine Fault and in areas adjacent to active faulting, warm springs with associated gases are common. Elsewhere in the South Island, less easily classified gases occur in Fiordland (H_2 -rich) and in Otago (CO_2 -rich).

The isotopic data, sampling details and partial chemical analyses are listed in tables 1 and 2. Three of the samples, listed as "Barnes" in Table 1 represent the results published by Barnes et al. (1978). Most He isotope data are from Giggenbach et al. (1993). The chemical analyses show that most of the gases are CH_4 -rich, but some are N_2 -rich or CO_2 -rich. The Poison Bay seep consists predominately of H_2 ; 710 mmole/mole (Lyon & Giggenbach, 1990).

Recent reviews of many overseas natural gases (Schoell, 1980, 1983, 1988) provide some guidelines for the interpretation of the isotopic compositions of CH_4 -rich gases and allow the analytical data to be related to the genesis of the gases. The characterisation is based largely on data for Europe and the USA (Schoell, 1980), with only two gases each from Egypt and the Philippines. Smith et al. (1985) found, on the basis of the composition of Australian gases, that these Northern Hemisphere classifications are not necessarily applicable to the Southern Hemisphere. A summary of the Schoell classification, as described in more detail in Lyon et al. (1992), is shown in figure 2.

The only New Zealand oil and gas fields producing commercially are in Taranaki; their compositions provide useful references (Lyon, 1989). In figure 2, the methane C and H isotopic compositions of the Taranaki gas are superimposed on the classification by Schoell (1988) and outlined by a triangle. All these samples fit into the zone of thermogenic gases associated with condensates or oils. The Maui CH_4 is more enriched in ^{13}C and D than that from Kapuni, implying that the former has been derived from more mature sediments, assuming similar source material.

The stable isotope data for the South Island are plotted in figures 3 and 4 along with the compositional areas for most New Zealand geothermal (Lyon & Hulston, 1984) and Taranaki gases, (cf figure 2). The samples from the South

Island have $\delta^{13}\text{C}(\text{CH}_4)$ values spanning the range from isotopically light microbial gases to heavier geothermal CH_4 , with few having values in the same range as those from Taranaki.

Relative N_2 , He and Ar contents are plotted in figure 5. All samples are enriched in He with respect to atmospheric gases. Where replicate samples have been collected, the least air-contaminated sample is plotted. The stable isotopic composition of He, measured as the ratio $^3\text{He}/^4\text{He}$ with respect to air, R_A , provides information on its origin (Giggenbach et al., 1993). For samples with low $^3\text{He}/^4\text{He}$ ratios ($<0.5 R_A$), the excess He is likely to be derived largely through radioactive decay of U and Th in the crust; for those with higher $^3\text{He}/^4\text{He}$ ratios ($>2.0 R_A$) considerable contributions from the mantle are indicated (Giggenbach & Goguel, 1989; Giggenbach et al., 1993). N_2/Ar ratios vary due to air-contamination during sampling, but also due to addition of N_2 through decay of organic material, or, less likely, addition of ^{40}Ar from radioactive decay of K. High N_2/Ar values are found for some gases from the Marlborough, Murchison and Westland sedimentary basins.

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

$$\text{C}_{2+} = (1 - \text{C}_1/\text{Y}_{\text{C}_n}) \times 100 \quad (3)$$

where C_n is the content of individual hydrocarbons $\text{C}_n\text{H}_{2n+2}$, for $n = 1$ to 5; C_1 is the content of CH_4 . Low C_{2+} values are typical of immature and overmature stages of oil/gas generation. Migration is considered to preferentially remove higher hydrocarbons (Schoell, 1983), and therefore to reduce C_{2+} with little or no effect on the isotopic composition of CH_4 . A detailed study of Japanese natural gases by Igari & Sakata (1988) showed that natural gases tend to lose their C_2 to C_4 hydrocarbons during migration in the order: n-butane $>$ propane $>$ i-butane $>$ ethane $>$ methane.

Higher hydrocarbon analyses (C_2 to C_6) are available for most of the samples and for some Taranaki gases (Giggenbach, unpublished results). Figure 6 shows the relationship between $\delta^{13}\text{C}(\text{CH}_4)$ and C_{2+} . The maximum value of C_{2+} of about 13% contrasts with data for Taranaki gases which show values up to 31%. The highest value here was found for the Blackwater gas flame. The data in figure 6 conform to the generalisation in Schoell (1983) that gases with the highest C_{2+} have $\delta^{13}\text{C}$ values in the range -50 to -35‰.

The relationships among some of the hydrocarbons (the alkanes C_1 - C_6) are shown in figure 7 for one sample from each site together with data for a McKee (MK) well (which had $\text{C}_{2+} = 13.4\%$) shown for comparison. This McKee sample has a pattern very similar to that of the other Taranaki gases from Maui and Kapuni. In this plot, migration as reported by Igari & Sakata (1988) would tend to cause three changes: move the line downward, straighten the line and steepen the part joining the higher hydrocarbons. By contrast, microbial attack on gases in groundwaters would be expected to be most destructive on the CH_4 and lighter hydrocarbons and thus move the line upwards and make it more horizontal.

Sedimentary basin gases

Marlborough In this area, considered to be the southern extension of the North Island East Coast deformed belt, mid to late Cretaceous strata rest with marked unconformity on a deformed basement of Torlesse sediments (Laird, 1992,

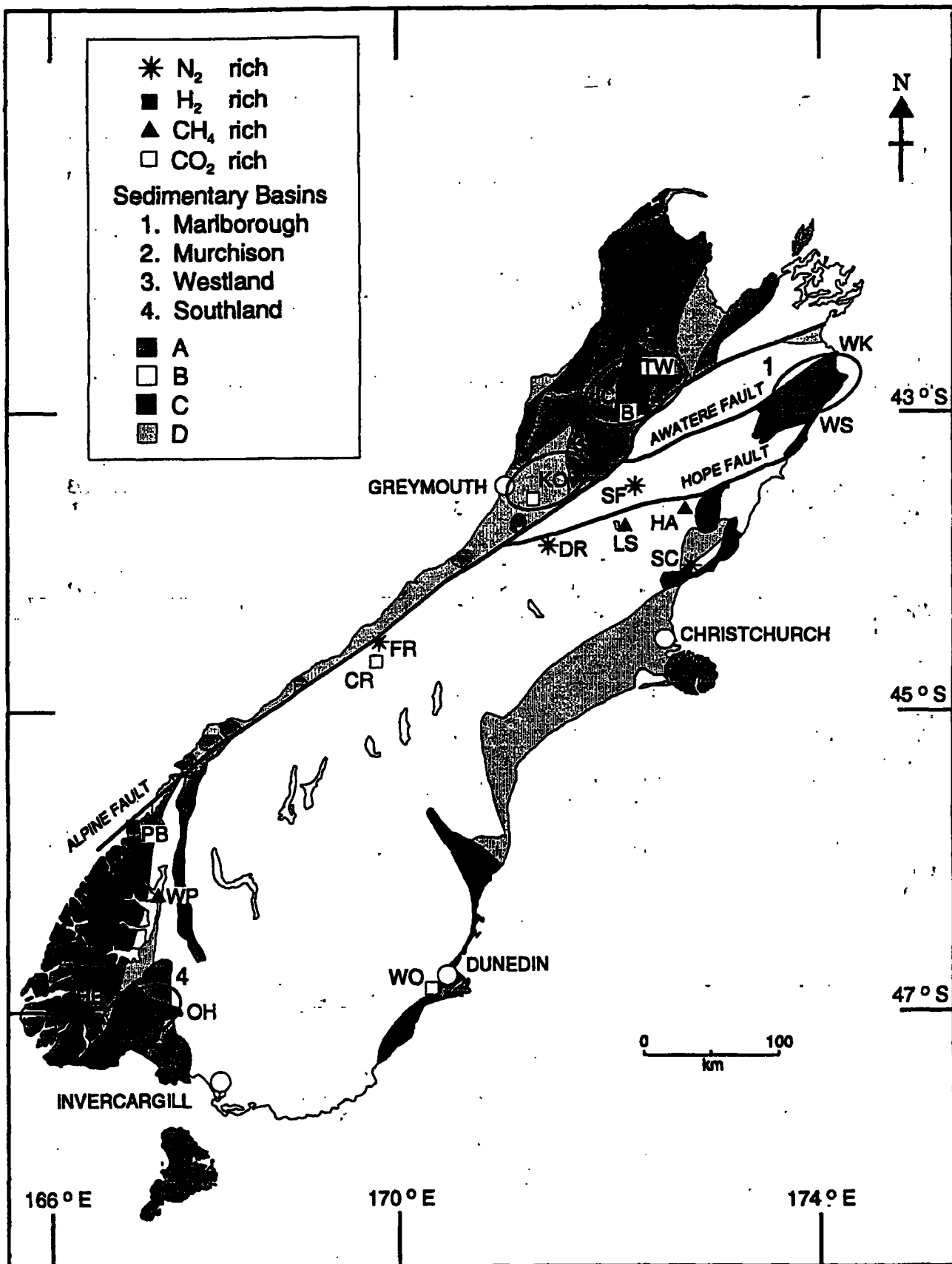


Fig. 1. Map of the South Island of New Zealand showing generalised geology and sample sites. Site labels are as in table 1.

- A. Igneous rocks and Palaeozoic sediments
- B. Torlesse group and other greywacke and schists
- C. Cretaceous and Tertiary sediments
- D. Quaternary sediments

Table 1. Gas sample details.

Site	Name	Grid Ref NZMS 260	Sampling Date	Temp. °C	Analysis No.	Sample R No.
WS	<i>Marlborough</i> Wharf Stream	P30/850175	02-Feb-93		524	18207/1
WK	Waireka #1	P29/936404	04-Feb-93	16	525	18207/2
WK	Waireka #2	P29/936404	04-Feb-93	16	526	18207/3
	<i>Murchison</i>					
TW	Te Wiriki	M29/683347	04-Feb-93	10	529	18207/6
B1	Blackwater #1	M29/607235	03-Feb-93		527	18207/4
B2	Blackwater #2	M29/607235	03-Feb-93		528	18207/5
JC	Johnson Cr	M29/514272	02-Feb-90	13	386	14049/7
	<i>Westland</i>					
KO	Kotuku R	K32/838522	03-Feb-90	22	380	14049/1
KO	Kotuku well	K32/838509	03-Feb-90	22	381	14049/2
KO	Kotuku 3	K32/838509	03-Feb-90	22	384	14049/5
	<i>Southland</i>					
HB	Hindley Burn 1.	C45/863548	15-Sep-89		340	11850/1
HB	Hindley Burn 3	C45/863548	15-Sep-89		342	11850/3
OH	Ohai, coal gas	D45/174632	01-Apr-85	25	133	11106/37
	<i>Fiordland</i>					
PB	Poison Bay 1	C40/853011	14-Sep-89		334	11848/1
PB	Poison Bay 2	C40/853011	14-Sep-89		335	11848/2
WP	Welcome Point	D41/031477	15-Sep-89		339	11849
	<i>Fault Gases</i>					
LS	Lake Sumner	L32/320343	Barnes			
SF	Sylvia Flats	M32/596577	02-Feb-90	53	390	14049/10
HA	Hanmer #2	N32/958539	02-Feb-90	52	387	14049/8
HA	Hanmer #1	N32/958539	02-Feb-90	52	389	14049/9
HA	Hanmer Springs	N32/958539	Barnes			
SC	Scargill	N33/001065	01-Feb-90	14	385	14049/6
DR	Deception R	K33/981190	12-Feb-90	33	392	14049/12
FR	Fox R	H35/689431	05-Feb-90	38	391	14049/11
CR	Copland River	H36/636264	05-Feb-90	59	382	14049/3
CR	Copland River	H36/636264	Barnes			
WO	Wairongoa	I44/049827	10-Feb-90	13	383	14049/4
WO	Wairongoa	I44/049827	01-Nov-87		263	11642/7

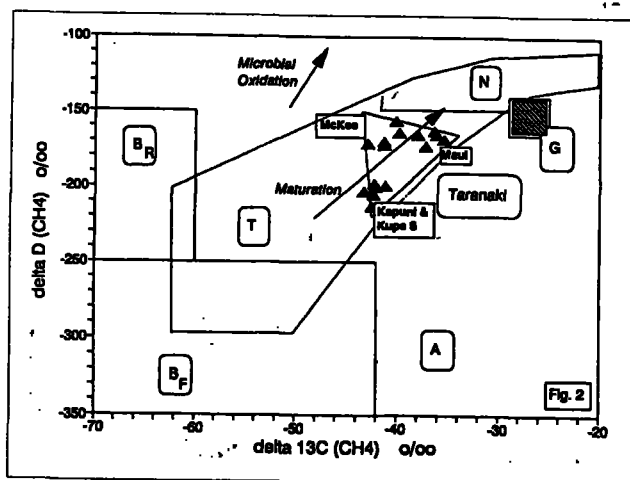


Fig. 2. Deuterium and carbon-13 values for naturally occurring methane and processes (after Schoell, 1988). B_R = microbial gases produced from reduction of carbon dioxide, B_F = microbial gases derived from fermentation processes. G = most New Zealand geothermal gases (from Lyon & Hulston, 1984). N = thermogenic gases not associated with oils, T = thermogenic gases associated with oils and condensates. A = abiogenic methane. Data for Taranaki commercial oil and gas fields from Lyon (1989) and Lyon (unpublished).

Lensen, 1963). Tertiary and Quaternary tectonics have produced a number of active faults and high relief.

The Waireka gas (WK) appears to discharge from the boundary of Torlesse sediments with Tertiary rocks on the NE side of the Haldon Hills. It is a very dry gas (figures 6,

7a) but its isotopic composition places it in the middle of the thermogenic range (figure 4). By contrast, higher hydrocarbon contents are much higher (figures 6 and 7a) in the Wharf Stream (WS) gas, reportedly from Upper Cretaceous sediments (McLernon, 1978). The CH_4 is very heavy isotopically (figure 4), suggesting that it is derived from over-mature sediments. However the high N_2/Ar value confirms the origin as being from organic-rich sediments. Blue Mountain gas blow (not analysed for this report) lies

Table 2. Chemical and isotopic data.

Site	Name	CO ₂	N ₂ mmole/mole	CH ₄	C ₂₊ %	δ ¹³ C(‰)		δD‰ CH ₄	³ He/ ⁴ He x R _A
						CO ₂	CH ₄		
WS	<i>Marlborough</i> Wharf Stream	0.5	8.5	988	1.98		-31.7	-136	1.14
WK	Waireka #1	1.3	37.7	960	0.008		-40.9	-149	
WK	Waireka #2	2.3	101	894	0.009		-42.4	-126	
	<i>Murchison</i>								
TW	Te Wiriki	1.6	15.7	980	9.0		-38.6	-149	0.16
B1	Blackwater #1	0.13	7.9	990	13.1		-43.1	-167	0.33
B2	Blackwater #2	18	181	787	11.7		-42.5	-165	
JC	Johnson Cr	11	110	866	0.23		-44.6	-172	2.57
	<i>Westland</i>								
KO	Kotuku R	860	100	35	3.09	-3.2	-55.5	-196	
KO	Kotuku well	934	25	41	2.46	-3.9	-47.5	-221	3.60
KO	Kotuku 3	867	36	93	0.36	-6.1	-47.1	-198	
	<i>Southland</i>								
HB	Hindley Burn 1	0	17.6	978	0.47		-67.8	-193	0.03
HB	Hindley Burn 3	0	15.5	982	0.37		-67.6	-175	0.03
OH	Ohai, coal gas	6	3	998	0.17		-58.7	-206	0.06
	<i>Fiordland</i>								
PB	Poison Bay 1	0.4	54.3	244	0.31		-36.4	-325	3.90
PB	Poison Bay 2	0.09	23.3	264	0.29		-36.3	-330	3.87
WP	Welcome Point	281	9	710	0.001	-8.9	-60.0	-295	1.23
	<i>Fault Gases</i>								
LS	Lake Summer	0	420	570			-38.2	-137	
SF	Sylvia Flats	11.9	668	309	0.088		-31.6	-120	0.16
HA	Hanmer #2	1.1	100	894	0.077		-36.9	-157	0.87
HA	Hanmer #1	0.6	669	327	0.063		-36.5	-155	
HA	Hanmer Springs	0	60	930			-36.1	-160	
SC	Scargill	9.7	511	461	0.012		-48.4	-133	0.07
DR	Deception R	0.5	852	135	0.052		-38.7		0.06
FR	Fox R	275	553	163	0.033	-9.7	-38.0	-151	0.65
CR	Copland River	935	49	14	0.017	-8.8	-33.0	-138	0.43
CR	Copland River	960	30	10			-32.8	-115	
WO	Wairongoa	961	34	3.6	0.20	-7.3	-37.5	-168	6.81
WO	Wairongoa	951	43	2.3	0.18		-39.7	-150	6.64

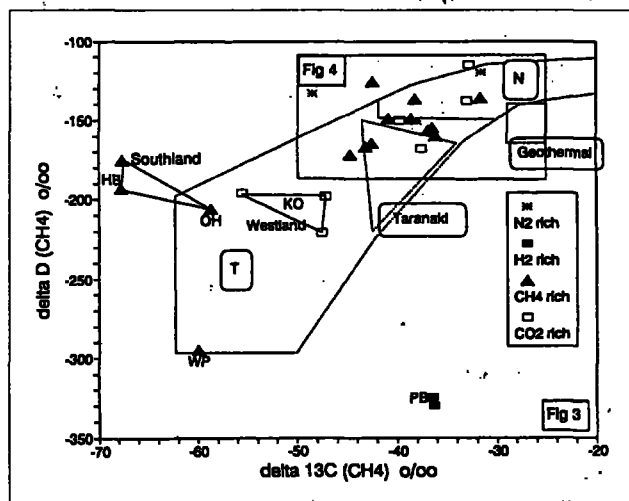


Fig. 3. Deuterium and carbon-13 values for South Island methane together with compositional areas of geothermal and Taranaki gases. Site labels as in table 1 and figure 1.

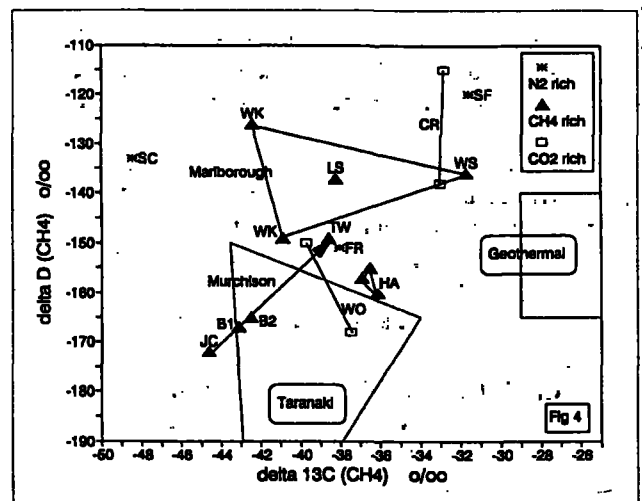


Fig. 4. Enlargement of area marked in figure 3. For site labels see figure 1.

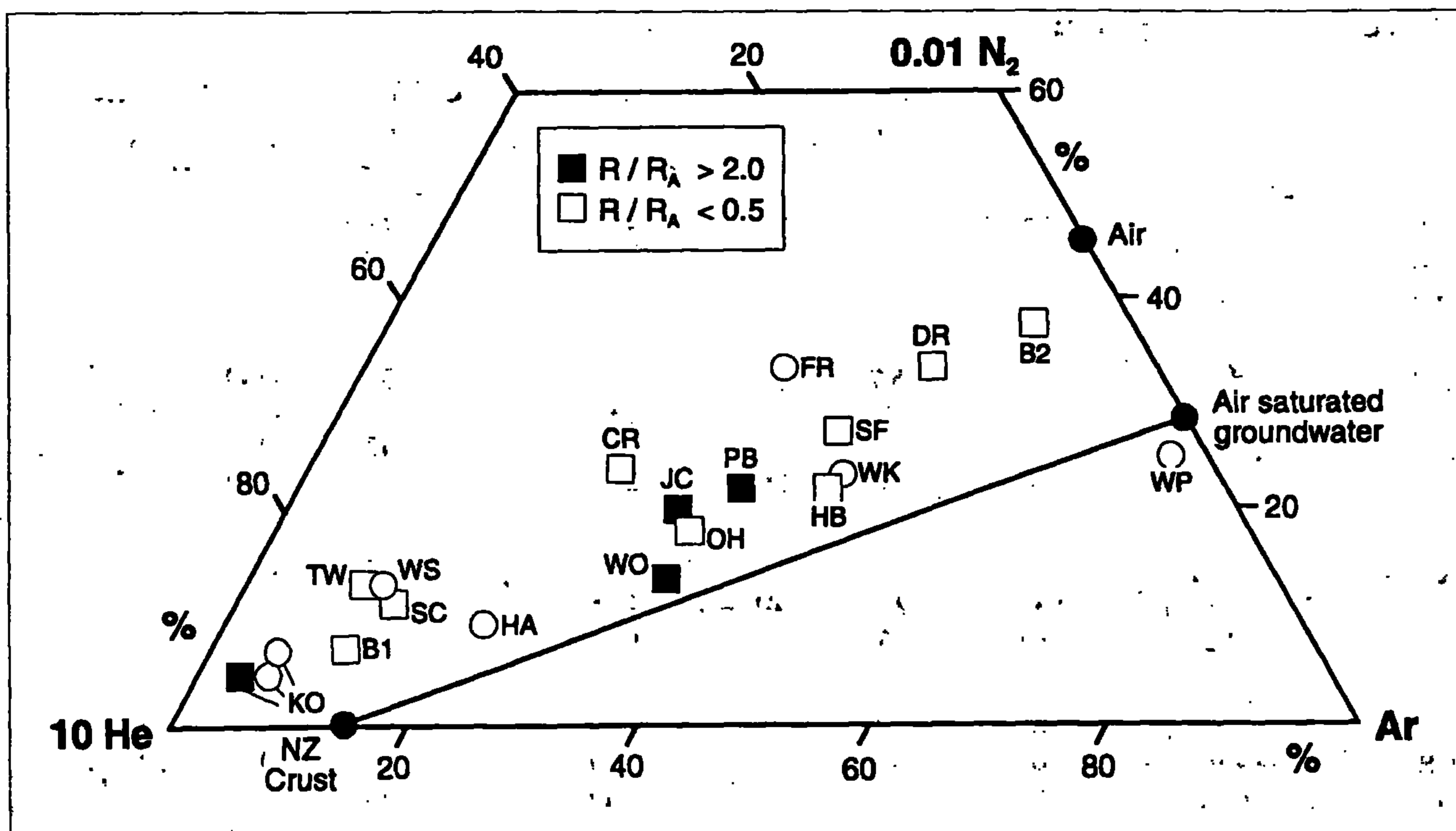


Fig. 5. South Island gas N_2 -He-Ar relationships for air-free samples from each site. Site labels as in figure 1.

very close to the Clarence Fault at its north-east extremity (Browne, 1992). Russell (1959) considers that both Wharf Stream (WS) and Blue Mountain gases are produced from Upper Cretaceous mudstone.

Murchison Basin This basin lies adjacent to a major bend in the Alpine Fault, and includes a late Eocene to late Miocene succession, up to 8 km thick, but highly deformed (Crundwell, 1990, Suggate, 1984). There are a number of oil and gas seeps and some wells were drilled before 1985. Likely source rocks are the Brunner Coal Measures and overlying Eocene and Miocene carbonaceous sediments. In figures 6 and 7a, Johnson Creek is shown to have the lowest relative content of C_{2+} . This agrees with the earlier study of Crundwell (1990) who showed that the proportions of higher hydrocarbons increase from Johnson Creek in the west (JC, Storm Creek in Crundwell, 1990) to Blackwater (B1, B2) to Te Wiriki (TW) in the east.

The above trends are reflected in the CH_4 isotopes where figure 4 shows Johnson Creek on the less mature side of Taranaki gases, Blackwater being similar to McKee field gases and Te Wiriki (TW) isotopically more enriched and therefore from a more mature source. The smooth relationship is likely to reflect different degrees of maturity of otherwise similar source rocks for all three discharges. Te Wiriki gas has less higher hydrocarbons than does Blackwater (figure 7a), and the relative enrichment of n-butane suggests migration has been more significant at Te Wiriki.

Ratios of $^3He/^4He$ decrease from a high value of $2.6 R_A$ for Johnson Creek (JC) over $0.33 R_A$ at Blackwater (B1) to $0.16 R_A$ at Te Wiriki (TW) indicating decreasing addition of mantle He. The Johnson Creek gas is associated with a brine of similar chemical and isotopic composition to Morere on the East Coast, North Island. In this case, the fluids are possibly formed through expulsion of seawater entrapped in subducting sediments with an enrichment in 3He due to cosmic particles as suggested by Anderson (1993) or a

possible admixture of mantle volatiles (Giggenbach et al., 1993). The comparatively rapid rise of mantle gases over the western part of the Murchison Basin may be facilitated by deep fracturing associated with these highly compressional environments (Koons & Craw, 1991). The increased incidence of earthquakes in this area (Reyners, 1989) may also favour transport of mantle gases through seismic pumping or fault-valving as proposed by Sibson (1990). The chemistry of the two Blackwater samples shows that (B2) may have been altered by the entrainment of combustion gases from the flame present at the time of sampling in 1993.

Westland The Kotuku oil seep (KO) is located inland from Greymouth in the Westland Basin. The oil and gas seep from Quaternary sands and gravels which overlie Oligocene Cobden Limestone and the Cretaceous Paparoa Coal Measures (Matthews, 1990, Nathan et al., 1986). These gases (figures 6, 7b) contain high proportions of higher hydrocarbons as might be expected from their association with oil, but have a pattern much more horizontal than the McKee oil field gas, probably reflecting the biodegradation seen in the associated oil (Nathan et al., 1988). However, the C and H isotopic composition of the three gases analysed from this site are very depleted in heavier isotopes suggesting low levels of maturity. This is not inconsistent with the findings of Smith et al. (1985) that $\delta^{13}C$ values don't necessarily relate to maturity for gases from coals. The Kotuku well gas, like those from Johnson Creek in the Murchison Basin and the Maui Field offshore Taranaki, has an unusually high $^3He/^4He$ ratio of $3.6 R_A$ (Giggenbach et al., 1993) which cannot be explained by any of the usual source processes related to active magmatism. The Kotuku gases have high proportions of CO_2 . Matthews (1990) reports that a nearby CO_2 'geyser' was a well which drew on water and gas from the Cobden Limestone but contained no oil. The oil seeps (with low CO_2), were therefore considered to have been sourced stratigraphically above the limestone. This

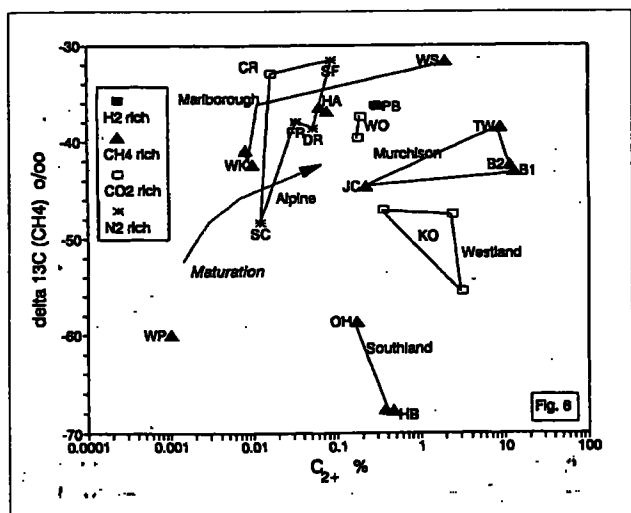


Fig. 6. Variations in $\delta^{13}\text{C}(\text{CH}_4)$ with higher hydrocarbon content, C_{2+} in %. For site labels, see figure 1.

limestone could be the source of the CO_2 , which occurs with the hydrocarbons ($\delta^{13}\text{C}$ values about -4‰).

Southland Basin The two gases from the Waiu Basin of Western Southland (Turnbull et al., 1993) are from a natural seep in the Hindley Burn (HB) and from a pressurised gas well drilled into the Ohai coal deposit (OH). The negative values for CH_4 , with $\delta^{13}\text{C} < -60\text{‰}$ indicate a low maturity microbial source. However, Smith et al. (1985) showed that the isotopic composition of Australian (and probably also other Southern Hemisphere) coal-derived gases do not fit the pattern of Schoell (1983) based on empirical evidence from mostly Northern Hemisphere marine-derived natural gases. Gases from coals exhibit a wide range of compositions, overlapping with the Waiu Basin values. The Hindley Burn gas is possibly derived from a formation similar to the late Cretaceous Ohai coals in the western part of the basin. These sub-bituminous coals, however, are not exposed nor reached by the only well in this part of the basin, Happy Valley-1. The basin has structures indicating that adequate maturity for oil production should exist in this area (Uruski & Turnbull, 1990). A possible alternative source is the immature Orepuki Oil Shale (late Eocene to Oligocene) exposed in the S of the basin. It would be a good source if it extended northwards (Turnbull et al., 1993). Both these gases have very low $^3\text{He}/^4\text{He}$ values (0.03 and $0.06R_A$) corresponding to a purely crustal origin of the He.

Non-basin gases

Fiordland The Poison Bay gases have been discussed in some detail earlier (Lyon & Giggenbach, 1990, Giggenbach et al., 1993) and the dominance of H_2 and the isotopic composition of the CH_4 are shown to be due to reduction of carbon in the adjacent ultramafic rocks, with a minor contribution from carbon in groundwater.

In extreme contrast to the Poison Bay gas, the Welcome Point gas seep is entirely biological, emanating from groundwater saturated buried sediments in the delta of the Eglinton River, as indicated by the isotopic compositions of C and H (Lyon & Giggenbach, 1990). Radiocarbon dating indicates that the vegetation source is post-1960 and the He isotopic composition indicates that He is derived from air-saturated groundwater.

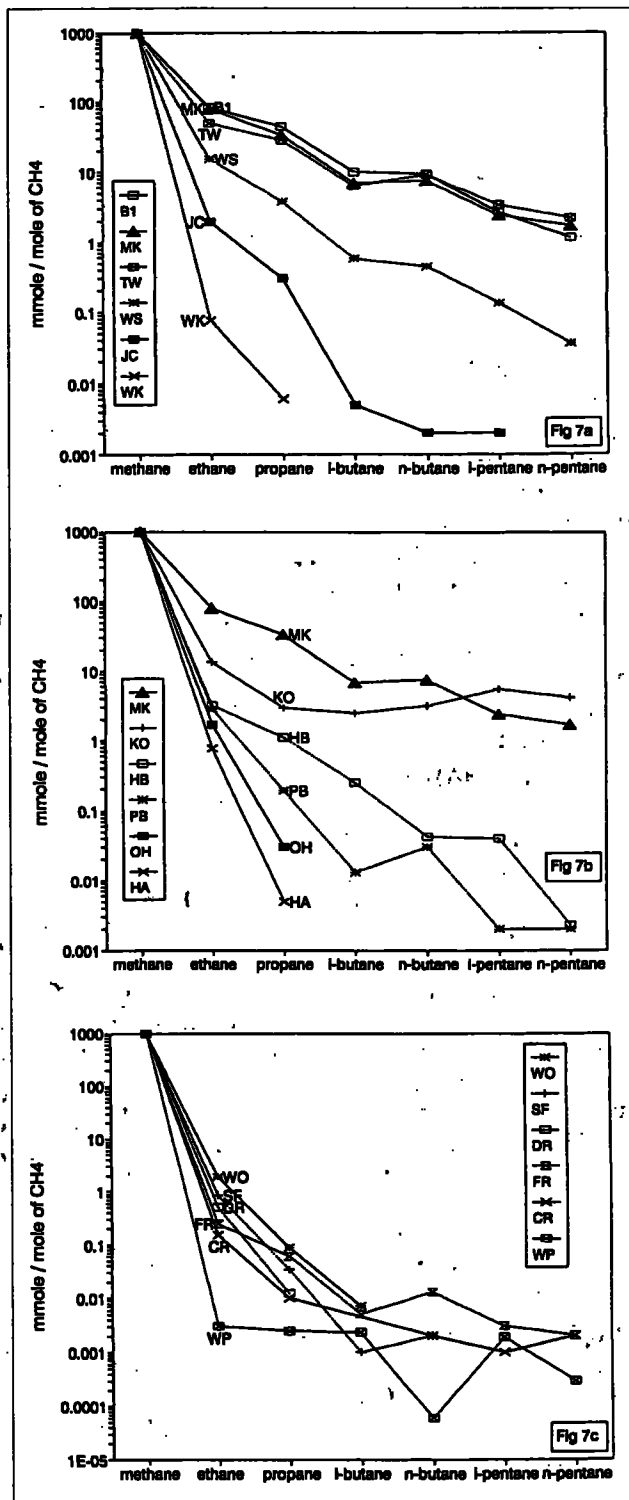


Fig. 7. Higher hydrocarbon relationships.

7a. McKee gas (MK) with gases from Marlborough (crosses) and Murchison (squares) sedimentary basins.

7b. Other high methane gases including Southland (squares) and McKee (MK).

7c. Low methane gases (with extended scale).

Fault gases The Wairongoa gas from the north-west margin of the Taieri Plains, a tectonic depression in Eastern Otago, has a $^3\text{He}/^4\text{He}$ ratio of about $6.7R_A$, a value typical of gases from the Taupo Volcanic Zone (Giggenbach et al., 1993). The most recent volcanic activity in the area is mid-to-late-Miocene. On the basis of an empirical geochronometer, derivation of the gas from very recent (<3 Ma) basaltic rock

with some CO₂ loss was suggested (Giggenbach et al., 1993). The $\delta^{13}\text{C}$ value of the CO₂ is not incompatible with a magmatic source, and the isotopic composition of the CH₄ (figure 4) indicates that it could have come from the adjacent Torlesse group greywackes, although the large difference between the two samples is unexplained.

All the other gases are near the Alpine Fault or related to major transcurrent faults. They dominate the tectonics of the South Island, and represent the trace of a horizontal shift of a belt of Permian rocks by >500 km and vertical rates of uplift of >10 mm/a (Allis, 1986).

The North Canterbury gas seeps at Deception River (DR), Lake Sumner (LS) and Sylvia Flats (SF) are high in N₂, and the CH₄ isotopic compositions of Sylvia Flats gas and of Copland River (CR) are enriched relative to most other samples indicating microbial oxidation. All have a low C₂₊ contents (figures 6, 7c). The Hanmer (HA) and Scargill (SC) gases are both high in CH₄, but N₂ dominates in some of the other samples. The Scargill gas emanates with sulphate-rich waters, probably derived from shales and its ³He/⁴He ratio is low. Its $\delta^{13}\text{C}$ and δD values (figure 4) suggest low-grade thermogenesis. Field et al., (1989) report that most parts of this area have suitable source rocks that would be able to generate hydrocarbons, given sufficient burial.

Hanmer Springs (HA) is located in a minor basin (Field et al., 1989) adjacent to the Hope Fault, the southernmost branch of the Alpine Fault system. Gases issue at high flow, being collected and used for heating in the nearby Queen Mary Hospital. Using the ⁴⁰Ar/³⁶Ar value of 760 for Hanmer reported by Torgerson et al. (1982), Giggenbach et al. (1993) suggest a long residence time in the crust for this gas, but the fraction of mantle He is suggested to be still 11%. The $\delta^{13}\text{C}$ and δD compositions of the Hanmer gas, point to derivation from Torlesse greywackes, being almost identical to those from the Mangatainoka and Awakeri warm springs of the North Island axial ranges. This agrees with early theories reported in Field et al. (1989) who also surmise, however, that such gases would have been unlikely to survive the Rangitata Orogeny and that the hydrocarbons were more likely to have migrated into the Torlesse from overlying Cretaceous and Tertiary sediments, facilitated by fracture cleavage in the Torlesse rocks.

The Copland River (CR) gas is CO₂-rich and the gas at Fox River (FR) also has significant CO₂, compared to the other "alpine" fault gases where CO₂ is minor. The Copland River warm springs discharge dilute Cl-HCO₃ waters (Barnes et al., 1978) and both seeps have relatively low ³He/⁴He ratios (Giggenbach et al., 1993), although well above those expected for purely crustal gases. The gases are best explained as being flushed out of the rocks by deeply circulating groundwaters, the generation of permeability being due to active faulting, and the elevated temperatures due to rapid uplift bringing higher temperature rock to shallow levels (Allis et al., 1979). The CH₄ isotopic values in the gases from Deception River, Fox River and Lake Sumner are similar to those from the greywacke ranges of the North Island (Lyon et al., 1992), and most of the 'alpine' gases emanate from similar greywacke rocks.

Conclusions

Based purely on the isotopic compositions of CH₄ ($\delta^{13}\text{C} = -50$ to -35‰ , $\delta\text{D} = -220$ to -120‰), gases from South Island sedimentary basin are largely of thermogenic origin

and may be arranged, in increasing maturity, from Southland to Westland (Kotuku), through Murchison to Marlborough. The Murchison gases show a smooth progression in maturity from west to east. This increase in maturity is accompanied by an increase in C₂₊ contents from 0.2 to 13% and a decrease in ³He/⁴He ratios from 3.6 R_A to 0.16 R_A pointing to widely varying conditions of hydrocarbon formation from west to east.

Higher hydrocarbon contents (ethane to propane) reach 13% of total hydrocarbon for the eastern gases of the Murchison Basin and 2 to 3% for Kotuku in the Westland, and Wharf Stream in the Marlborough Basins.

The isotopic compositions of CH₄ for most of the non-basin gases, e.g. those produced along the Alpine Fault, also fall within the ranges of the basin gases suggesting similar formation conditions. Exceptions are some microbially oxidised low-CH₄ gases with $\delta^{13}\text{C}$ values near -32‰ and the H₂-rich gases from Poison Bay in Fiordland with much lower δD (-325‰) values, respectively, reflecting unusual formation conditions.

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Authors

GRAEME LYON is a graduate of Otago University where he majored in chemistry before obtaining a PhD in biogeochemistry at Massey University. Since 1969, he has worked on applications of stable isotope measurements at what is now the Nuclear Sciences Group of the Institute of Geological and Nuclear Sciences. His main areas of study have been in analysis of geothermal and natural gases in order to understand processes that are involved in generating and altering the compositions of gases. In addition he has worked in a wide range of applications of stable isotope geochemistry to food, agriculture, archaeology and environmental sciences.

WERNER GIGGENBACH is a geochemist of international reputation leading the understanding of geothermal and volcanic fluid chemistry. He received his university education in Munich, Germany, and has worked since 1968 at DSIR Chemistry before transferring into the Institute of Geological and Nuclear Sciences. His primary interest is to delineate the origins and histories of terrestrial fluids and what they tell us about geological processes.