

CARBON AND HYDROGEN ISOTOPIC COMPOSITIONS OF METHANE FROM NORTHLAND AND WEST WAIKATO

Graeme L Lyon
Institute of Nuclear Sciences, DSIR, Lower Hutt, New Zealand

Methane emanations from this region have widely varying isotopic compositions which reflect the geological settings and probable origins of the gases. None are closely similar to Taranaki natural gases.

The gases at Te Maire (Waikato), Parakai (Hélenesville), and a well near Waimamaku (Northland) are clearly of shallow origin, evolving methane produced by microbial reduction of CO₂ in buried sediments. Gas at Waingaro hot springs appears to be a mixture of microbial methane and thermogenic methane.

Northland gases are generally carbon dioxide rich, except for that at Wekaweka. Using Schoell's empirical classification, the methane isotopic compositions imply that they are similar to thermogenic dry gases, i.e., natural gases which are not associated with oil. The gases from Runaruna, Tangowahine and Wekaweka are all accompanied by saline, isotopically enriched waters. They thus appear to be the result of metamorphism of sedimentary rocks past the mature state for oil production, and subsequent tectonic processes are driving out these evolved connate waters and gases.

The Waiwera, Kamo and Mangamuka samples are very low in methane and have highly enriched isotopic values, suggesting that they have been further altered by microbial oxidation. This has probably occurred in the local aquifer.

INTRODUCTION

There are a large number of places in New Zealand where gases seep naturally from the ground. Many of these have been reported from well-known and obscure localities and their analyses recorded by Ross (1967) and McLernon (1978) but until recently few modern analyses had been made. The springs of Northland (or North Auckland) and Waikato have had recent reviews by Petty (1972), Mongillo and Cleland (1984) and Petty et al. (1987). These include warm and cold mineral springs, many with gas accompanying the water flow.

The geology of this area (Fig. 1) is complex. Greywacke and argillite of Permian to Jurassic age underlie most of the region, with Cretaceous and Tertiary rocks overlying much of the greywacke basement. The Tertiary Northland Allochthon is widespread north of Auckland. This includes sandstones, mudstones, limestones and a few thin coal seams. Several groups of Cenozoic volcanic rocks, some of which are Quaternary, intrude and overlie the older sediments. Quaternary tectonic activity and sea-level changes have allowed recent sediments to accumulate in some locations.

The waters and gases that emanate from the ground are extremely variable in composition. Only at the Ngawha geothermal field (Fig. 1) have they been studied in detail (Browne et al., 1981; Lyon and Hulston, 1984; Mongillo, 1985). Summaries of some of the chemistry of waters and gases have been collated by Petty (1972) and Petty et al. (1987), but do not include any isotopic analyses.

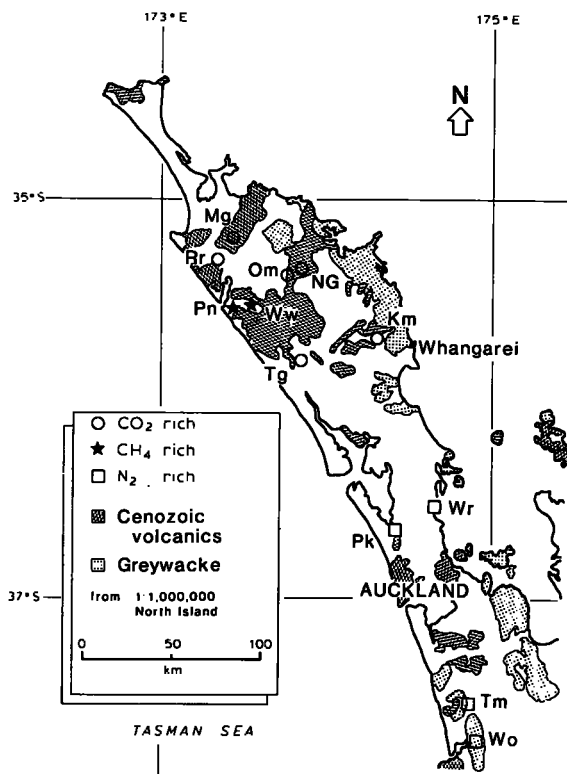


Fig. 1: Location of the sample sites, North Island, New Zealand.

This study concentrates on the carbon-13 (^{13}C) to carbon-12 (^{12}C) ratio, and deuterium (D or ^2H) 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}C and hydrogen, ^3H (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 δD values, in parts per thousand (‰)

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

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

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 here. The characterisation is based on the data listed in Schoell (1980) of which most are from the USA and Europe, with two 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 ‰ (Fig. 2). Dry gas, with small or negligible amounts of ethane, can form during microbial, anaerobic diagenesis at temperatures less than 70 °C. If reduction of carbon dioxide occurs then carbon isotopic fractionation is greatest and the methane is very depleted in ^{13}C , i.e. $\delta^{13}\text{C}$

values less than about -55 ‰ . In 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.

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}C , and also in D (Coleman *et al.*, 1981; Whiticar and Faber, 1986).

The only New Zealand oil and gas fields producing commercially are in Taranaki and these provide useful examples of the use of the isotopic technique (Lyon, 1989). Fig. 3 is a plot of the methane carbon and hydrogen isotopic compositions of the Taranaki gas superimposed onto a classification from Schoell (1988). All these samples fit into the zone of gases associated with condensates or oils. The Maui methane is more enriched in ^{13}C and D than is methane from Kapuni, which implies that the Maui gas has been derived from more mature sediments than the Kapuni gas, assuming similar sediments. Pilaar and Wakefield (1984) show that the Western Platform has lower maturity levels observed in the sediments than are found in the Graben Complex. The isotope data is therefore evidence that Maui gas has migrated from much deeper levels.

The McKee field CH_4 including McKee, Tuhua and Toetoe wells, is also shown to be derived from more mature sediments than Kapuni, with more enriched isotopic composition. But possibly its relationship to the oil with which it is associated, moves it into a different part of the diagram, to more negative $\delta^{13}\text{C}$ values than is the case for Northern Hemisphere associated gases. This diagram shows that related gases are easily identified.

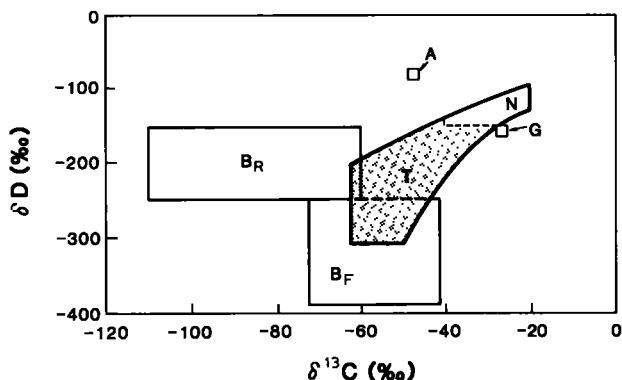


Fig. 2 : Deuterium and carbon-13 values for naturally occurring methanes (from Schoell, 1988) A = atmospheric methane. BR = microbial (bacterial) gases produced from reduction of carbon dioxide. BF = microbial gases derived from fermentation processes. G = most New Zealand geothermal gases (from Lyon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

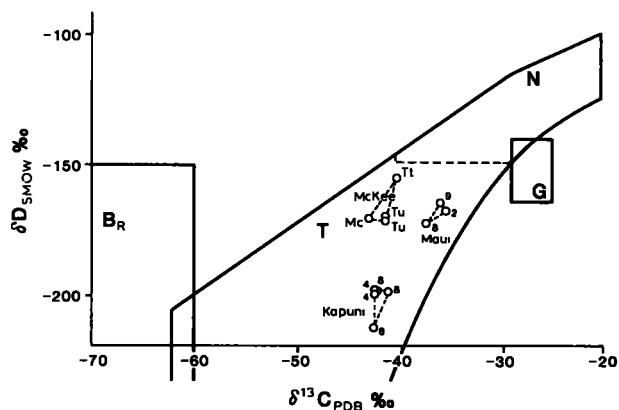


Fig. 3 : Deuterium and carbon-13 values for some Taranaki well gases plotted on an enlargement of part of Fig. 2. Symbols as for Fig. 2. McKee field includes wells from Toetoe, Tuhua and McKee as marked. Maui and Kapuni well numbers as marked.

METHODS

Sample collection

Gas samples were collected into evacuated glass bottles (Giggenbach, 1975). For samples dominantly carbon dioxide, flasks containing about 50 mL of 4 M sodium hydroxide solution were used, but hydrocarbon gases were collected into empty flasks of 300-400 mL capacity. Springs or seeps were generally sampled by inverting a funnel over the gas seep at the bottom of its water pool source if possible, and leading the gas to the flask through titanium and butyl rubber tubing.

Sample analysis

Chemical and mass spectrometric analyses were carried out as outlined in Lyon and Hulston (1984). For gases with $CH_4/H_2 > 200$, i.e. all except geothermal gases, oxidation of methane was by reaction of gas with copper oxide at 800 °C. The use of the liquid oxygen-cooled trap prior to oxidation, ensured that carbon dioxide, water, ethane and higher hydrocarbons were not let into the oxidation system. Since 1984 all deuterium analyses have been prepared by the *hot-shot* zinc method (Stanley *et al.*, 1984).

For methane, analytical precision for $\delta^{13}C$ is about $\pm 0.2 \text{‰}$, and for δD about $\pm 3 \text{‰}$.

RESULTS AND DISCUSSION

The data from isotopic analysis, sampling details and chemical analyses are listed in Tables 1 and 2. Fig. 1 shows the sites sampled for this study. The data are plotted in Fig 4.

The tables shows that a wide variety of localities and therefore of tectonic and geological settings were sampled. Temperatures varied from ambient to 64 °C, and water flows

varied from nil to many litres per second with the water varying from fresh water to saline brines. Most of the gases were rich in either methane or carbon dioxide, but none showed unusual or rare compositions such as helium-rich (as occur in the USA), or hydrogen-rich (such as the Zambales gas, Abrajano *et al.*, 1988).

Mangamuka

The most northerly spring is at Mangamuka where a carbon dioxide-rich fluid is flowing from Tangihua volcanic rocks (Petty *et al.*, 1987). The water is a bicarbonate solution with an isotopic composition similar to local meteoric water. Methane is only a trace component of the gas (0.04%), insufficient for a deuterium measurement. The methane and carbon dioxide $\delta^{13}C$ values are similar to values from Kamo where they are interpreted as gas from overmature sediments.

Runaruna

A mud volcano has formed at this spring site in Cretaceous mudstone (Petty *et al.*, 1987) on the crest of a hill where cold saline water has gas bubbling through it. The water is isotopically enriched (Downes *et al.*, 1980; Allis *et al.*, in prep.) and is consistent with being a metamorphic water, i.e. an evolved connate water being expelled from sediments undergoing diagenesis. Two isotopic analyses of gases are plotted in Fig. 4. One value is a composite of two incomplete analyses, the other a repeat 1987 collection. The methane is unusually enriched isotopically, placing it in the region of the non-associated methanes of Schoell (1988) but is more enriched than the coal gases of NW Germany (Schoell, 1980). Either it is derived from a high degree of overmaturity, or altered by oxidation since formation (Coleman *et al.*, 1981), or possibly by an unusually large migration effect.

Symbol	INS R.No.	Bottle No.	Name	Grid Reference		Collection Date	Temp °C	Comments and Collector
				NZMS1	NZMS260			
Mg	11641/1	8	Mangamuka	N10/995594	005/55671	87.04.19		WFG
Rr	9026/18	80	Runaruna	N14/855455	005/420548	79.11.28	18	Vent No 1 DSS/GLL
Rr	5137/6		Runaruna	N14/858457	005/423549	76.02.19	23	IB/CJD/JRH
Rr	11641/2	51	Runaruna	N14/855455	005/420548	87.04.20		WFG
Ww	9026/19	79	Wekaweka	N18/047151	006/588265	79.11.27	22	DSS/GLL
Ww	5137/8		Wekaweka	N18/048154	006/589268	76.02.19	22	IB/CJD/JRH
Pn	11545/1	45	Paniora's well	N18/936149	006/487266	83.09.09		Waimanaku Beach Rd, RBG
Om	5449/8		Omapere	N15/332403	P05/855488	77.06.28	30	G & L
Om	9134		Omapere	N15/332403	P05/855488	80.05		Geothermal Institute
Km	5137/4		Kamo	N20/808035	Q06/281139	76.02.18	23	IB/CJD/JRH
Km	11641/4	6	Kamo	N20/808035	Q06/281139	87.04.19	24	WFG
Tg	11641/3	38	Tangowahine	N19/370940	P07/878064	87.04.20	18	WFG
Wr	11641/5	134	Waiwera	N38/224971	R10/634157	87.04.19	45	WFG
Pk	464/4		Parakai	N37/957833	Q10/386037	58.		Helensville, H&M
Pk	11641/6	95	Parakai	N37/957833	Q10/386037	87.04.21	61	Helensville, WFG
TM	11274/2	W5	Te Maire	N51/460819	R13/820097	84.12.04	64	West Spring, Naikie, WFG
TM	11545/9	116	Te Maire	N51/460819	R13/820097	86.02.04	63	WFG
Wo	11641/7	136	Waingaro	N55/517584	R14/866882	87.04.18	53	WFG

Table 1: Sample sites and collection details for Northland and Waikato.

Symbol	Name	Collection Date	$\delta^{13}\text{C}_{\text{PDB}}$		δD	CO_2	CH_4	$\text{C}_2\text{H}_6/\text{CH}_4$	^3He
			CO_2	CH_4					
Mg	Mangamuka	87.04.19	-11.0	-28.2		99.5	0.12	0.17	
Rr	Runaruna	79.11.28	-6.7	-22.5		77.3	16.3	0.33	
Rr	Runaruna	76.02.19	-2.9		-137	76	17		
Rr	Runaruna	87.04.20	-7.0	-22.8	-116	96.8	1.8	1.7	
Ww	Wekaweka	79.11.27	-11.2	-30.3		15.4	74.8	0.13	
Ww	Wekaweka	76.02.19		-30.6	-140	20	71		
Pn	Paniora's well	83.09.09		-60.6	-185	0.01	92.7	0.73	
Om	Omapere	77.06.28	-5.5	-33.9	-171	96.4	1.62	0.23	
Om	Omapere	80.05	-7.8	-33.6	-143				
Km	Kamo	76.02.18	-10.5			99	0.4		
Km	Kamo	87.04.19	-10.6	-28.8	-127	99.4	0.39	0.02	
Tg	Tangowahine	87.04.20	-7.8	-32.2	-148	87.4	7.8	2.7	
Wr	Waiwera	87.04.19		-33.1	-26	0.03	14.7	0.03	
Pk	Parakai	58.		-58					
Pk	Parakai	87.04.21	-10.1	-57.7	-148	0.85	41.3	0.40	
TM	Te Maire	84.12.04		-63.0	-198	5.8	21.9	0.15	
TM	Te Maire	86.02.04		-62.3	-200	<0.02	19.8	0.19	0.45
Wo	Waingararo	87.04.18		-54.7	-162	0.61	5.5	0.01	

Table 2: Stable isotope composition of some natural gases from Northland and Waikato.

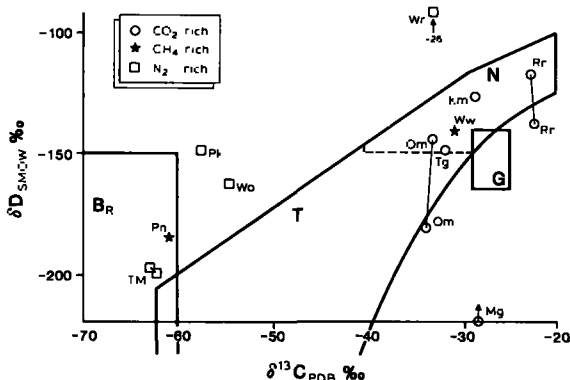


Fig. 4: Deuterium and carbon-13 values for Northland and West Waikato methane. Sample symbols as in Tables 1 and 2. Ngawha geothermal methane values plot within G. Other symbols as for Fig. 2.

Wekaweka

The Waimamaku valley, site of the deepest Northland exploration well Waimamaku-1 has the Wekaweka gas seep which was once used as a source of gas for heating and lighting. The cool saline water is isotopically enriched (Downes *et al.*, 1980) similar to Runaruna, but it flows from a pool in the valley through early Tertiary mudstone which is overlain on the valley hills by Tangihua volcanics. Methane is the dominant gas component, and Fig. 4 shows it is isotopically enriched relative to Taranaki gases. As with Runaruna gas, a post-mature source rock is suggested.

Paniora's well, about 10 km from Wekaweka has methane of completely different isotopic character, suggesting a microbial origin (Fig. 4). This is consistent with the well's shallow depth of 80 m in recent alluvial sediments near the mouth of the valley, and its low CO_2 content and low flow (R. B. Glover, DSIR, pers. com. 1984). This gas does, however, have a high ethane/methane ratio (Table 2), and could result from early thermochemical processes (Schoell, 1983), perhaps mixed with bacterial gas.

Omapere

The Omapere Spring is close to Lake Omapere, and 6 km northwest of Ngawha Springs and emits dilute bicarbonate water, and gas dominated by CO_2 (Giggenbach and Lyon, 1977; Sheppard and Lyon, 1981). It contains a much lower proportion of H_2S and H_2 relative to CO_2 than do the geothermal springs at Ngawha. Isotopically, the methane is lighter than geothermal gas.

The springs are in Quaternary sediments on the edge of Lake Omapere, but have the chemistry and isotopic composition of cold groundwater (Sheppard and Lyon, 1981). They are probably heated by geothermal activity related to the nearby Ngawha geothermal field and they flow from near to the Quaternary Te Pua andesites (Skinner, 1981).

Kamo

This vigorous, gassy spring, of cool temperature (24 °C) has been used to feed bathing pools. Eocene limestone and siltstone underlie the alluvial flats (Petty *et al.*, 1987). The water is bicarbonate-rich and isotopically similar to meteoric water (Allis *et al.*, in prep.). The gas is 99% carbon dioxide, similar to that at Mangamuka chemically and iso-

topically. The methane isotopic composition is very enriched, placing it on Fig. 4 in Schoell's zone of dry non-associated gases suggesting it results from overmature organic sediments. Perhaps this is from the flushing of buried Tertiary sediments or of the greywacke/argillite basement by the meteoric water or by the large volumes of carbon dioxide being evolved. The carbon isotopic composition of the carbon dioxide (-10.5‰) is similar at Kamo and Mangamuka and also at Parakai and some Hauraki warm springs (Lyon, 1989). Such a CO_2 composition is not readily explained but may be a mixture of magmatic CO_2 with soil derived CO_2 .

Tangowahine

These springs have small fluid flow and some are on ridge tops of mudstone in a similar setting to Wekaweka and Runaruna. The water and gas isotopic compositions of Tangowahine are very similar to Wekaweka but Tangowahine is carbon dioxide-rich rather than methane-rich. A similar origin, overmature sedimentary rock, is implied.

Waiwera

The Waiwera Hot Springs is a popular resort complex now fed by wells with measured temperatures of up to $48\text{ }^\circ\text{C}$. They are fed from a fault zone in the greywacke/argillite, the water rising through the overlying Waitemata Group sandstone and siltstones (Petty *et al.*, 1987). The water is saline but isotopically similar to meteoric water. The gas is nitrogen-rich with little carbon dioxide. The methane isotopic composition is unusual, being extremely enriched especially in deuterium, with $\delta\text{D} = -26\text{‰}$, $\delta^{13}\text{C} = -33.1\text{‰}$. The only likely explanation for the heavy hydrogen isotopic composition is subsurface partial oxidation by microbial action. Some anaerobic bacteria are able to oxidise methane readily (Coleman *et al.*, 1981; Whiticar and Faber, 1986). Isotopic enrichment of the remaining methane occurs as the isotopically light methane is preferentially oxidised. An extreme case of this occurs at Waitangi Soda Springs (Lyon, 1989) where the original unoxidised methane can be identified and the ratio of change of δD to change of $\delta^{13}\text{C}$ is about 8, similar to that in some laboratory experiments of Coleman *et al.* (1981). Extrapolation back to a reasonable δD value of -150 to -250‰ , implies a $\delta^{13}\text{C}$ value of about -50 to -60‰ for the unoxidised methane. This puts it near to the range of oil associated methanes, and similar to Waingaro methane.

Parakai

These hot springs near Helensville are believed to flow from faults in the underlying greywacke up through Tertiary sandstones and siltstones into the alluvial/marine sands (Petty *et al.*, 1987). The gas is mostly nitrogen and methane and the water is saline but isotopically closer to the meteoric water line than to the metamorphic waters of Runaruna, Wekaweka and Tangowahine (Allis *et al.*, in prep.).

The methane isotopic composition is similar to microbial methane produced from reduction of carbon dioxide, although some 30‰ more enriched in deuterium than the methane in Paniora's well. This suggests that perhaps the fluid in which reduction is occurring may be 30‰ more enriched, i.e. at Parakai near to sea water composition rather than meteoric water, and that it is produced from the shallow sediments rather than the greywacke. There has been no

change in $\delta^{13}\text{C}$ value of the methane since the 1958 collection of Hulston and McCabe (1962).

Te Maire

The hot water springs at Te Maire (Naike) rise through alluvial sediments probably from the underlying greywacke (Petty, 1972). As at Waiwera, the gas is dominantly nitrogen. The methane isotopic compositions of two different samples are identical and indicate that the methane is of microbial origin, thus is probably being stripped from the shallow sediments by the upflowing warm water which is of meteoric isotopic composition and only weakly mineralised ($213\text{ mg kg}^{-1}\text{ Cl}$). The helium isotopic ratio of $^3\text{He}/^4\text{He} = 0.45 R_A$ indicates mostly crustal gas with little deepseated helium-3 input (Sano *et al.*, 1987).

Waingaro

The Waingaro springs are only 20 km south of Te Maire in a similar geological setting of north and northeast trending faults in greywacke and argillite. There is a large flow (5.7 L s^{-2} ; Petty, 1972) of $53\text{ }^\circ\text{C}$ water with similar isotopic composition to that at Te Maire. The methane isotopic composition is more enriched than usual for microbial methane such as at Te Maire, and suggests there may be some thermogenic methane mixing with a bacterial gas.

General

Although this paper is not able to study the chemistry of the gases and waters in any detail, some clear trends are obvious. The gases in the northern parts of Northland are generally dominated by carbon dioxide as shown in Fig. 1. Wekaweka and Paniora's well are exceptions, being methane rich gases. The most southerly samples are all from warm springs and are nitrogen-rich.

Nitrogen-rich gases are not common world-wide, but some have been recently studied in California (Jenden *et al.*, 1988). However, the most nitrogen-rich gases in the California Great Valley, were also those with methane that was enriched isotopically, to $\delta^{13}\text{C}$ values about -20‰ . That is quite different to those here, which have $\delta^{13}\text{C}$ values less than -50‰ (except for Waiwera which is oxidised).

The carbon dioxide-rich gases are not all the same isotopically. Mangamuka and Kamo gases are both 99% CO_2 and their $\delta^{13}\text{C}$ values, of CO_2 and CH_4 are similar (Fig. 5) suggesting similar sources. However those carbon dioxide are isotopically distinct from Runaruna and Tangowahine which are similar to each other. The two latter gases are also similar to Omapere and to Ngawha geothermal gases, and the isotopic values of -6 to -8‰ are generally considered to be in the range of magmatic gases.

There thus appears to be a flux of deepseated carbon dioxide of two different compositions to the surface in northern Northland. Their cause and origin are unknown.

There is also the possibility that, especially at high temperatures, there has been able to be isotopic equilibration between carbon dioxide and methane. Fig. 5 shows the theoretical temperatures implied if this were to occur, and, as Lyon and Hulston (1984) show, these are higher than measured temperatures in geothermal areas, e.g. at Ngawha measured maximum temperatures are $200\text{--}230\text{ }^\circ\text{C}$. However, Lyon and Hulston (1984) show that these temperatures

REFERENCES

- ABRAJANO, T.A.; STURCHIO, N.C.; BOHLKE, J.K.; LYON, G.L.; POREDA, R.J. and STEVENS, C.M. 1988: Methane-hydrogen gas seeps, Zambales ophiolite, Philippines: deep or shallow origin. In: M. Schoell (Guest-Editor): "Origins of Methane in the Earth", *Chemical Geology* 71, 211-222.
- ALLIS, R.G.; STEWART, M.K. and GIGGENBACH, W.F. In preparation: Review of New Zealand hot springs and their implications for fluid movement in the crust.
- BROWNE, P.R.L. et al. 1981: The Ngawha Geothermal area. *DSIR Geothermal Report 7*. DSIR Science Information Division, Wellington.
- COLEMAN, D.D.; RISATTI, J.B. and SCHOELL, M., 1981: Fractionation of carbon and hydrogen isotopes by methane-oxidizing bacteria. *Geochimica et Cosmochimica Acta* 45, 1033-1037.
- DOWNES, C.J., HULSTON, J.R. and BARNES, I., 1980: Stable isotope and chemical studies of warm springs of North Island, New Zealand (Extended Abstract) *Proceedings of the Third International Symposium on Water-Rock-Interaction, Edmonton*, 188-189.
- GIGGENBACH, W.F., 1975: A simple method for the collection and analysis of volcanic gas samples. *Bulletin Volcanologique* 39, 132-145.
- GIGGENBACH, W.F., 1982: Carbon-13 exchange between CO_2 and CH_4 under geothermal conditions. *Geochimica et Cosmochimica Acta* 46, 159-165.
- GIGGENBACH, W.F. and LYON, G.L., 1977: The chemical and isotopic composition of water and gas discharges from the Ngawha geothermal field, Northland. N.Z. DSIR Chemistry Division unpublished report: File 30/555/7-WFG.
- HULSTON, J.R. and McCABE, W.J., 1962: Mass spectrometer measurements in the thermal areas of New Zealand Part 2. Carbon isotopic ratios. *Geochimica et Cosmochimica Acta* 26, 399-410.
- JENDEN, P.D.; KAPLAN, I.R.; POREDA, R.J. and CRAIG, H., 1988: Origin of nitrogen-rich natural gases in the California Great Valley: evidence from helium, carbon and nitrogen isotope ratios. *Geochimica et Cosmochimica Acta* 52, 851-861.
- LYON, G.L., 1989: The stable isotope composition of some North Island natural gases. *Ministry of Energy Report No RD8807*. 26 pages.
- LYON, G.L. and HULSTON, J.R., 1984: Carbon and hydrogen isotopic compositions of New Zealand geothermal gases. *Geochimica et Cosmochimica Acta* 48, 1161-1171.
- McLERNON, C.R. 1978: Indications of petroleum in New Zealand: NZ Geological Survey unpublished open file Petroleum Report No 839.
- MONGILLO, M.A. (Compiler) 1985: The Ngawha Geothermal Field: new and updated scientific investigations. *DSIR Geothermal Report 8*.

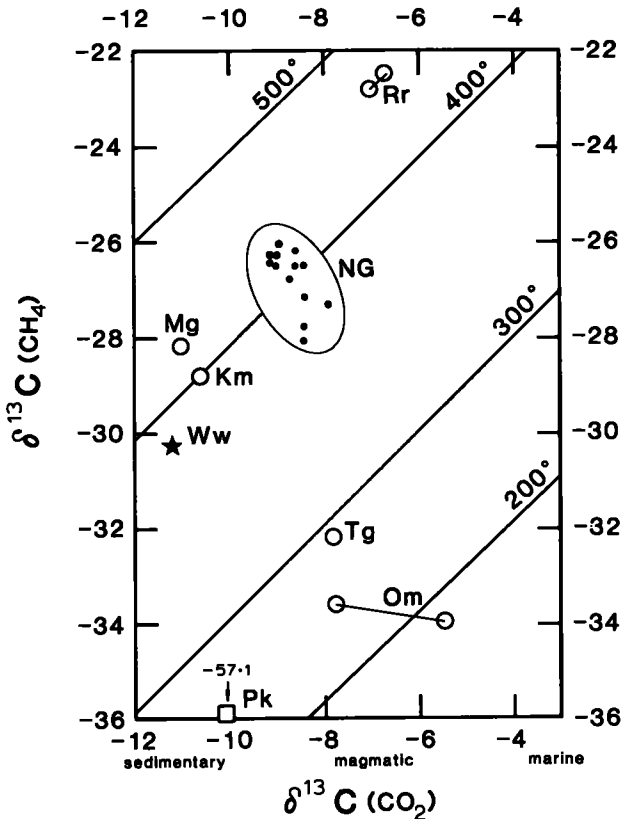


Fig. 5: Carbon-13 values for methane and carbon dioxide from Northland. NG = Ngawha geothermal field. Temperatures are those estimated from isotopic equilibration (see Lyon and Hulston, 1984). Other samples do not have enough carbon dioxide for analysis.

may be useful in a relative way, although Giggenbach (1982) suggests that unreasonably long times would be needed for equilibration.

If we use Fig. 5 with the above reservations, then the inferences are that gases from Mangamuka, Kamo, Wekaweka and Runaruna may have experienced temperatures perhaps 100-200 °C higher than the gases from Tangowahine and Omapere. This may be a measure of the maximum depth of the source rocks of these gases.

CONCLUSION

This wide range of geological situations that gives rise to methane in the warm and cold springs of Northland and West Waikato is reflected in the variation of the stable isotopic composition of the methane. However the isotopic composition, often in conjunction with the chemistry of the gas and associated water can give indications of the likely subsurface conditions which give rise to individual gases.

ACKNOWLEDGEMENTS

For the sampling data and chemical information of most samples, I thank Dr W.F. Giggenbach, Chemistry Division, DSIR, Private Bag, Petone. Some information from Dr C.J. Downes and others of Chemistry Division, is gratefully acknowledged. The Ministry of Energy (Agreement 87/38) are thanked for their funding for most of the stable isotope analyses, and permission to use that data.

- MONGILLO, M.A. and CLELLAND, L., 1984: Concise listing of information on the thermal areas and thermal springs of New Zealand. *N.Z. DSIR Geothermal Report 9*, 226 pages.
- PETTY, D.R., 1972: Springs of the Auckland region. *NZ Geological Survey Report 57*.
- PETTY, D.R.; BROWN, L.J. and HOMER, D.L. 1987: *Mineral and thermal waters and springs of North Auckland*. NZ Geological Survey, Lower Hutt.
- PILAAAR, W.F.H. and WAKEFIELD, L.L. 1984: Hydrocarbon generation in the Taranaki Basin, New Zealand. In: *Petroleum Geochemistry and Basin Evaluation. AAPG Memoir 35*, 405-423.
- ROSS, J.B., 1967: Naturally occurring gases in New Zealand. DSIR Chemistry Division Report CD 6014.
- SANO, Y.; WAKITA, H. and GIGGENBACH, W.F., 1987: Island arc tectonics of New Zealand manifested in helium isotope ratios. *Geochimica et Cosmochimica Acta 51*, 1855-1860.
- SCHOELL, M., 1980: The hydrogen and carbon isotopic composition of methane from natural gases of various origins. *Geochimica et Cosmochimica Acta 44*, 649-661.
- SCHOELL, M., 1983: Genetic characterization of natural gases. *American Association of Petroleum Geologists Bulletin 67*, 2225-2238.
- SCHOELL, M., 1988: Multiple origins of methane in the earth. In: M. Schoell (Guest-Editor), *Origins of Methane in the Earth. Chemical Geology 71*, 1-10.
- SHEPPARD, D.S. and LYON, G.L. 1981: 6. Chemistry of the Ngawha thermal area. In: Browne et al. *The Ngawha Geothermal Area. DSIR Geothermal Report 7*, 95-128.
- SKINNER, D.N.B. 1981: Geological setting and sub-surface geology of Ngawha. In: BROWNE et al. *The Ngawha Geothermal Area. DSIR Geothermal Report 7*, 14-35.
- SMITH, J.W.; RIGBY, D.; GOULD, K.W.; HART, G. and HARGRAVES, A.J., 1985: An isotopic study of hydrocarbon generation processes. *Organic Geochemistry 8*, 341.
- STANLEY, K.; LYON, G.L. and STEWART, M.K., 1984: Hot shot reduction of water to hydrogen for isotopic analysis. INS Report INS-R-322, 11 pages.
- WHITICAR, M.J. and FABER, E., 1986: Methane oxidation in sediment and water column environments - isotope evidence. *Organic Geochemistry (Advances in Organic Geochemistry 1985) 10*, 759-768.