THE ISOTOPE GEOCHEMISTRY OF HOT SPRING GASES AND WATERS FROM COROMANDEL AND HAURAKI

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SUMMARY - Carbon, hydrogen and oxygen stable isotope analyses have been made on carbon dioxide, methane and water from warm and hot springs in the Coromandel Peninsula and Hauraki Plains. Most of the waters are isotopically unaltered meteoric waters. Methane $\delta^{13}C$ values vary widely, from -30 ‰ to -72 ‰. Warm springs in swamps at Maketu and Kerepehi have microbial methane probably added to the water near the surface. Puriri, Okoroire and Miranda springs produce thermally derived methane. The Kaitoke springs at Great Barrier Island and Te Aroha springs also contain thermally derived methane, and the Hot Water Beach gas is similar to the Kaitoke gas in chemistry and isotopic composition but altered by shallow microbial oxidation. The Te Aroha gas, though, is not inconsistent with a geothermal origin and the boiling springs and oxygen-isotope altered water are further evidence for high temperatures. Other spring gases have mixtures of thermogenic and microbial methane and none are closely similar to major NZ geothermal CH_4 compositions. CO_2, which is usually present in lesser amounts than N_2, has isotopic values which suggest a geothermal origin at Te Aroha and Maketu, but otherwise indicates a crustal origin. The dominance of N_2 implies that the fluid flows are tectonic fracture flow rather than geothermal. $^3He/^4He$ data gives further evidence of no major contribution from magmatic material except at Maketu, on the NW boundary of the TVZ.

1. INTRODUCTION

There are a considerable number of places in the Coromandel Peninsula, Great Barrier Island, and the Hauraki area, when warm or hot springs have been observed (Mongillo and Cleland 1984). Some geological and geophysical reports (e.g. Petty 1972, Hochstein and Nixon 1979, New Zealand Geological Survey 1974) outline the possible geological and structural reasons for the locations of these springs. This report looks at the stable isotope compositions of the fluids from many of these springs, and combined with some chemical information allows further interpretation of the significance of these springs.

The geological setting of the area of this study (Fig. 1) includes the Coromandel Peninsula and Great Barrier Island mountains dominated by Miocene and Pliocene volcanics, mainly andesites but including rhyolites and a few basalts. This activity continued into the Quaternary at Mayor Island. The Hauraki Plains are a down-faulted zone with several springs on hypothesised faults within and at the sides of the plains, which consist of Quaternary sediments bounded on the west by Waipapa greywacke.

The isotopic compositions of the gases are useful indicators of their genesis. Variations in carbon and hydrogen isotopic ratios of methane have been related to their origins in the summary papers of Schoell (1983, 1988). In New Zealand, natural gas isotopic ratios were collated by Lyon (1989) and a more detailed consideration of Northland and West Waikato gas seeps in comparison with Taranaki natural gases was made by Lyon (1990). Geothermal gas isotopic compositions have been considered in Lyon and Hulston

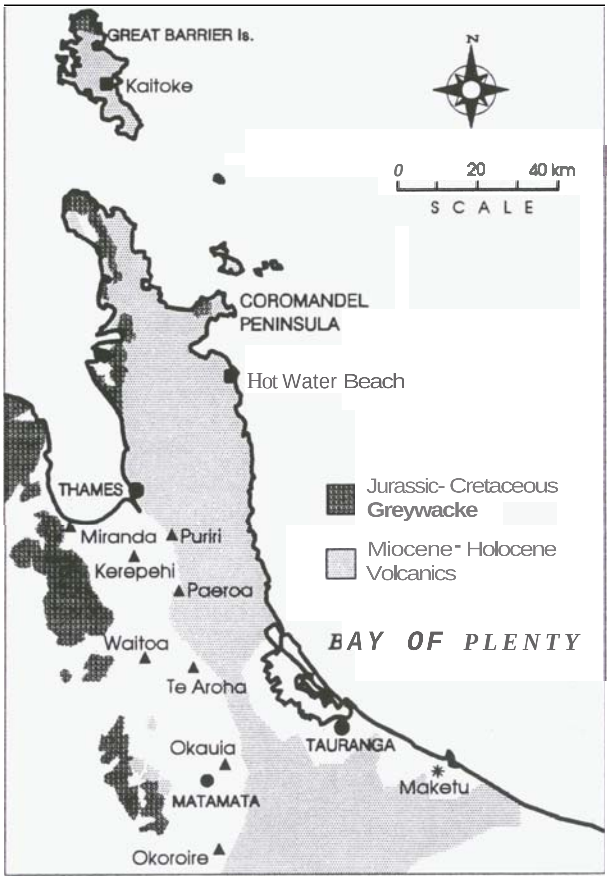

Figure 1: Map of the Hauraki-Coromandel area showing spring sites and simplified geology.

Table 1. Gas Sampling : Sites and Analyses

Blank spaces indicate no data available.

Site Label	Sampling Date	Name	Grid Ref. NZMS 260	N.S. R No.	delta 13C (o/oo) CO2	delta 13C (o/oo) CH4	delta D (o/oo) CH4	3He/4He R/Rair	CO2 mole % dry gas	CH4 mole % dry gas	N2 mole % dry gas
		Coromandel									
Kt	10-Mat46	Kaitoke Spring	S08/290503	11414/2	-13.6						
Kt	10-Mar46	Kaitoke Spring, Left	S08/290503	11414/1	-13.2	-34.3	-123	0.55	30.3	22.6	45.8
HW	08-Jan-87	Hot Water Beach	T11/620753	11414/3	-13.3	-30.1	-95	0.54	30.0	1.0	67.0
		Hauraki									
Mi	07-Dec-84	Miranda	S12/171410	1127411		-40.2			5.2	24.6	68.6
Mi	04-Feb-86	Miranda	S12/171410	11545/10		-40.1	-137	*0.92*	<0.1	27.3	71.4
Mi	10-May-79	Miranda	S12/171410	5919/9		-40.2	-145		19.3	23.0	56.8
Ke	04-Feb-86	Kerepehi	T12/365321	11545/11	-9.1	-66.8	-212	*0.32*	31.9	50.2	17.7
Wt	10-May-79	Waitoa	T13/386073	5919/7	-11.9	-54.0	-177		50.0	22.3	27.0
Pi	26-Apr-89	Puriri Soda Spg	T12/450367	11781/7	-9.9	-35.3	-129	0.88	99.6	0.1	0.1
Pa	16-Feb-76	Paeroa 1	T13/456222	5137/9	-10.6	-54.6	-170		89.0	5.8	4.6
TA	16-Feb-76	Te Aroha	T13/504025	5137/1	-7.2	-30.1			94.0	1.5	4.1
	10-May-79	Okauia Crystal Spg	T14/601756	5919/5	-17.7	-51.4			1.2	6.0	91.0
Oa	10-May-79	Okauia Opal Pool	T14/601756	5919/6	-8.3	-51.7	-137		1.4	6.0	91.0
Oa	25-Apr-89	Okauia Opal Pool	T14/601756	11781/6	-16.8	-50.8	-119	1.15	14.0	4.5	81.0
Ok	10-May-79	Okoroire	T15/566574	5919/4	-14.4	-50.6	-122		1.7	10.8	85.5
Ok	24-Mays5	Okoroire	T15/566574	11545/4	-11.2	-35.4	-145	1.35	7.0	8.0	84.0
		Bay of Plenty									
Mk	26-May-70	Maketu	V14/132754	2784/1	-7.1	-70.4	-240		0.7	*85.0*	13.5
Mk	11-May-79	Maketu	V14/132754	5919/8		-70.9	-227				
Mk	05-May-89	Maketu	V14/132754	11781/8	-11.6	-64.0	-186	6.50	25.0	71.0	3.0

1984), **where it is** shown that the **isotopic fractionation** between **methane** and **carbon dioxide may give** *useful* **temperature** estimates for **geothermal** *springs.*

2. METHODS

2.1 Sample Collection

Gas samples were **collected** into evacuated glass bottles **(Giggenbach 1975).** For samples dominantly composed of carbon dioxide, flasks containing about 50 mL of 4 M sodium hydroxide solution were used. 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.

2.2 Sample Analysis

Chemical and mass spectrometric analyses were *carried* out as outlined in Lyon and Hulston (1984) and Hulston *et al.* (1981). *All* **deuterium analyses are** now prepared by the hot-shot zinc method (Stanley *et al.* 1984). Analytical **precision is generally** ±0.2 ‰ for $\delta^{13}C$ values, ±0.15 ‰ for $\delta^{18}O$ and ±2 ‰ for δD values, in **the international** convention where $\delta^{13}C$ values **are** relative to PDB and δD and $\delta^{18}O$ values relative to SMOW.

3. RESULTS

The locations and brief description of all *springs* sampled are listed in Tables 1 and 2, and the locations shown in Fig. 1. The gas stable isotope and some chemical data are in Table 1, and **the** water isotope data are listed in Table 2. The isotope data are plotted in Figs 2-4.

Table 2. Stable Isotope Compositions of Waters

Site Label	NS No.	Sample Site	Sampling Date	Temp. deg C	del 18O o/oo	del D o/oo
		Coromandel				
Kt	MS26	Kaitoke hot spg	30-Sep-78	50	-4.01	-19.1
Kt	MS27	Kaitoke hot spg	30-Sep-78	50	-4.32	-21.8
Kt	MS131	N Peach Tree h s	08-Mar-86		-3.93	-22.3
Kt	MS132	Kaitoke hot spg	08-Mar-86		-4.58	-28.3
Kt	MS133	Kaitoke hot spg	09-Mar-86		-3.79	-22.1
Kt	MS134	Kaitoke hot spg	10-Mar-86		-4.54	-29.5
Kt	MS135	Kaitoke hot spg	10-Mar-86		-5.17	-30.0
Kt	MS136	S Peach Tree h s	10-Mar-86		-3.64	-19.3
Kt	MS137	Kaitoke Left	11-Mar-86		-4.17	-22.6
HW	MS40	Hot Water Beach, Orua	1979		-5.62	-30.2
HW	MS138	Hot Water Beach, Orua	08-Jan-87	55	-5.72	-31.2
		Hauraki				
Mi	MS30	Miranda h s	10-May-79	57	-5.87	-34.1
Mi	MS42	Miranda h s	1979		-5.57	-29.5
Ke	MS39	Kerepehi h s	01-May-79		-5.67	-31.5
Ke	GCO4	Kerepehi h s	1977	54	-6.24	-34.4
Wt	MS31	Waitoa h s	10-May-79	54	-5.81	-35.8
Wt	GCO1	Waitoa h s	1977	50	-5.71	-34.1
Pi	MS34	Puriri soda spg	11-May-79	17	-5.77	-34.4
Pi	MS181	Puriri		17	-5.75	-36.5
Pa	MS19	Paeroa	1976	18	-5.96	-33.3
TA	MS11	Te Aroha mineral spg	1976	19	-7.14	-38.2
TA	MS12	Te Aroha h s	1976		-224	-32.2
TA	MS43	Te Aroha-Mokeua Geyser	1979		-251	-31.9
TA	MS44	Te Aroha cold #15	1979		-2.58	-32.1
Oa	MS29	Okauia - Opal	10-May-79	39	-6.08	-33.1
Oa	MS45	Okauia - Opal spg	1979		-5.86	-35.8
Oa	MS46	Okauia - Crystal spg	1979		-5.79	-32.5
Oa	MS179	Okauia - Opal	25-Apr-89		-6.01	-34.9
Oa	MS180	Okauia well			-5.96	-34.9
Ok	MS28	Okoroire h s	10-May-79	38	-6.16	-35.5
Ok	MS48	Okoroire h s	1979		-6.25	-35.8
		Bay of Plenty				
Mk	2784/2	Maketu h s	26-May-70	49	-4.10	-312
Mk	MS33	Maketu h s	11-May-79	46	-5.13	-30.5
Mk	MS182	Maketu well	05-May-89		-5.38	-31.6

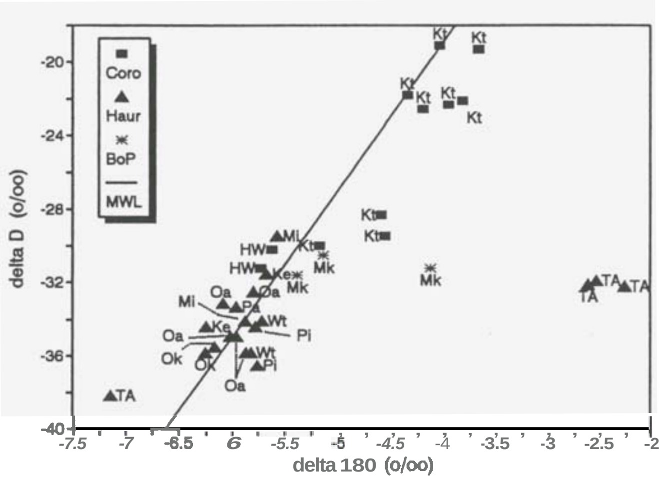

Figure *2:* Stable isotope ratios for waters. MWL is the meteoric water line $\delta D = 8.\delta^{18}O + 13$ (Stewart and Taylor 1981). Groupings and labels are as listed in Table *2;* symbols as in Fig. 1.

31 Kaitoke Springs (Kt), Hot Water Beach (HW)

The **Kaitoke** *springs* on Great Barrier Island and Hot Water Beach *are* both on the eastern side of the Tertiary volcanic rocks of Coromandel (**Moore** 1974, **Skinner** 1974). The stable **isotopic** compositions of all of these hot spring waters show that they are unaltered meteoric waters because they plot close to the line for North Island meteoric waters (**Fig. 2**). Many of the **Kaitoke** spring waters at *Great* Barrier Island show that they are more enriched in both deuterium and oxygen-18 than the **Coromandel** and Hauraki **waters** reflecting evaporation or a more oceanic influence.

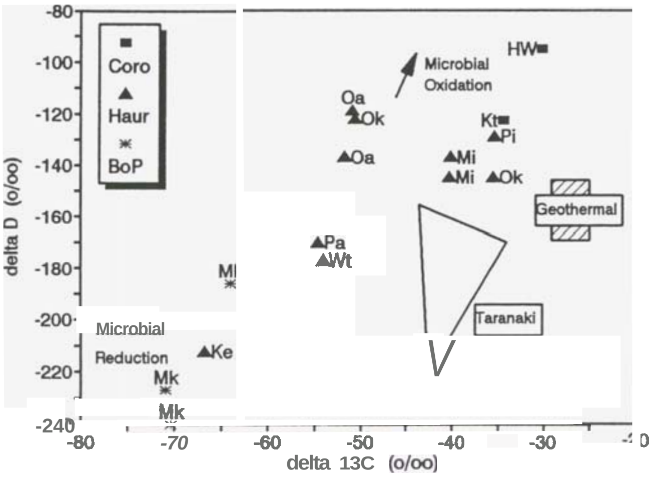

Figure 3: δD-$\delta^{13}C$ plot for methane. **The** rectangle for **geothermal gases** includes most samples from Tikitere, **Ngawha** and **Ohaaki** (**Lyon** and **Hulston** 1984), and the Taranaki triangle includes the natural *gas* **fields of Kapuni, Maui** and McKee (**Lyon** 1990); symbols are as in Fig. 1, labels as in Table 1.

At both sites, nitrogen is the major *gas,* with CO_2 the next most common gas constituent. The CO_2 $\delta^{13}C$ values at -13.2 ‰ *are* identical (Table 1, Fig. 4). Both gases too have identical $^3He/^4He$ **ratios** of 0.55 R_A (Giggenbach *et al.* in press), higher than in *crustal* gases probably due to extraction of some mantle ^3He from the Miocene volcanic rocks, also the probable *source* for the **carbon dioxide.** Both methane gases are unusually enriched in deuterium **and carbon-13** (**Fig. 3**), with the Kaitoke gas similar to the most enriched thermogenic **gases** of **Schoell (1988)** and the Hot Water Beach sample beyond that limit. This suggests the Kaitoke hot spring gases are derived from sediments that have been heated beyond the "oil window" **temperature** range *to* the over mature, *dry* gas stage. Another possibility, as indicated in Fig. 4, that they *could* be geothermal gases heated *to* **high temperatures (>300°C),** is rejected because geothermal gases *are* invariably **dominated** by CO_2. **High hydrocarbon** components are two to three orders of magnitude lower than Taranaki natural gases defining the dryness of the gas, but the presence of benzene is suggestive of a **geothermal** component.

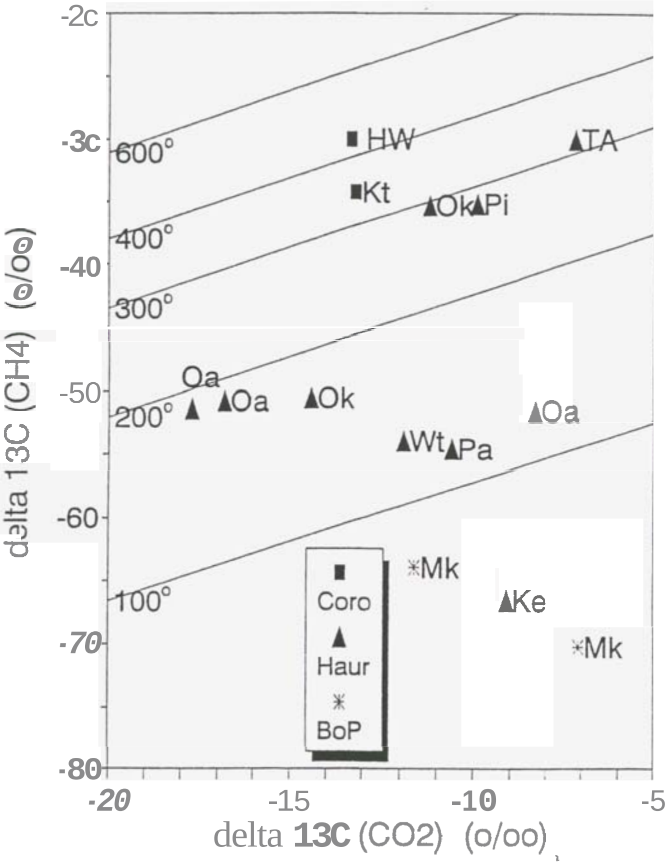

Figure 4: **carbon-13** values for CO_2 and CH_4, showing theoretical isotope equilibration temperatures in **degrees C** (from Lyon and **Hulston 1984**).

The Hot Water Beach methane could have been similar to the Kaitoke CH_4, but has been partially **oxidised,** *enriching* **both carbon and hydrogen isotopes. Such a shift could occur** if3096 of the methane was removed by microbial oxidation (Coleman *et* al. 1981) and the **chemical** composition shows that this gas does have a higher CO_2/CH_4 ratio than the **Kaitoke** gas (Table 1).

3.2 Miranda (Mi), Kerepehi (Ke), Waitoa (Wt) Springs

The Miranda warm spring area on the western side of the Hauraki Graben appears to be related to the boundary fault (Hochstein and Nixon 1979, *NZGS* 1974). The methane isotopes (Fig. 3) and low CO_2/CH_4 ratio suggest a thermogenic origin for the methane similar to Taranaki gases. The $^3He/^4He$ ratio is near atmospheric. The water isotopic ratios show that the springs are fed by meteoric waters, as is also the case at Kerepehi and Waitoa.

Hochstein and Nixon (1979) suggest: there must be a mid-graben fault separate from the western fault, and this allows warm water to circulate at Kerepehi. In the graben there is considerable depth (3 km) of sediment including peat deposits and thus it is not surprising that there is methane with an isotopic composition clearly indicating a microbial origin (Fig. 3). Recent activity on this fault is documented by de Lange and Lowe (1990). Kerepehi gas has a low CO_2/CH_4 ratio and very low amounts of hydrocarbons higher than ethane consistent with its microbial origin.

The Waitoa warm spring is also on the Kerepehi Fault (de Lange and Lowe 1990) but its gas composition is quite different to that at Kerepehi. It has a high CO_2 content, and the methane is less microbial in isotopic composition, than is Kerepehi CH_4. Its isotopic composition is halfway between ther compositions of Miranda and Kerepehi, suggesting a mix of microbial and thermogenic methane.

3.3 Puriri (Pi), Paeroa (Pa) and Te Aroha (TA) Springs

The Paeroa and Te Aroha samples were collected from cold mineral springs and their analyses discussed briefly by Downes et *al.* (1980). Puriri is also a cold soda spring, and all three gases are CO_2-rich. Paeroa methane appears to be a mixture of thermogenic and microbial methane similar to Waitoa, whereas Te Aroha CH_4 ($\delta^{13}C = -30$ ‰; sample was too small for δD analysis) may be partially oxidised or have a geothermal component from the nearby boiling springs in Te Aroha. Puriri methane is similar to the methane at Kaitoke, but present only as a very minor component. These springs are all on or near to the Hauraki graben eastern marginal fault. The high CO_2 contents, high carbon isotope equilibration temperatures (Fig. 4) and the high temperatures and oxygen-18 shifted water of some springs at Te Aroha (Fig. 2) *suggest* that these gases are geothermal in origin.

3.4 Okauia (Oa), Okoroire (Ok) Springs

These two hot spring areas are further to the southeast along the eastern marginal fault of the Hauraki graben, where it may be described as the western marginal fault of the Kaimai ranges. Stable isotope analyses show that all the waters are meteoric in origin (Fig. 2).

The methane isotope data (Fig. 3) *suggests* one of the Okoroire samples may have been a mislabelled Okauia gas. The three Okauia samples, $\delta^{13}C$ near -51% are unusually enriched in deuterium, which suggests they may have been subjected to partial oxidation by bacteria after mixing with warm oxygenated groundwater. This is *similar* to some other warm springs *such* as Waitangi Soda Spring (Lyon 1989) and some in the Salton Sea (Welhan 1988) and by experiments of Coleman et *al.* (1981). The Okoroire methane at $\delta^{13}C = -36\%$ shows that it is similar to the gas from Miranda. Both of these gases, from the western margins of the Graben, are nitrogen rich and could be derived from the greywacke. The chemical and isotopic compositions are similar to *gas* from the greywacke in western Hawke's Bay at Mangatainoka (Lyon *et al.* 1992).

3.5 Maketu (Mk) Springs

This warm spring area near the Bay of Plenty coast east of Tauranga is here considered as part of ther Hauraki-Coromandel region, following Mongillo and Clelland (1984). It is however on the NW edge of the Taupo Volcanic Zone. The gas is rich in methane which is isotopically light implying a microbial origin The stable isotope analyses of the waters (Fig. 2, and in Simpson and Stewart 1987) show they lie on the meteoric line except for one sample collected in 1970 which has an apparent 1 ‰ $\delta^{18}O$ shift. However, there is a high ^3He content ($R/R_A = 6.5$, Giggenbach *et al.* in press) and carbon dioxide $\delta^{13}C$ values are similar to *other* TVZ gases (Lyon and Hulston 1984), *showing* that geothermal gases are present with the microbial methane.

4 DISCUSSIONS AND CONCLUSIONS

The Hauraki-Coromandel warm and hot Spring gases are mostly nitrogen-rich (Table 1), with some being dominantly carbon dioxide and more typical of geothermal gases. The non-reactive gases all have *similar* N_2-Ar proportions to air, and with the significant addition of extra helium. He would be derived from uranium series elements radioactive decay to helium which could move readily into any water. Some of the samples also have had $^3He/^4He$ ratios measured (Sano et al. 1987; Giggenbach et *al.* in press). Okoroire and Okauia show slightly greater $^3He/^4He$ than in air but most are less than the air ratio, showing generally minor magmatic influence. The exception is Maketu where a high $^3He/^4He$ value reflects its location as part of the Taupo Volcanic Zone. Nitrogen-rich gases *occur* in several other places in the North Island (Lyon 1990, Lyon et *al.* 1992), and appear to be characteristic of warm *springs* issuing from faults in greywacke. The heat is thus not related to magmatic sources, but to tectonic activity and conducted to meteoric water *during* deep circulation in faults. The nitrogen and methane are derived from organic matter in buried sediments. None of these gases have significant amounts of hydrogen gas which is always present in fluids from high temperature geothermal fields.

The methane stable isotope ratios in Fig. 3 show a wide range of compositions, but none are closely similar to Taranaki natural gases or to New Zealand geothermal gases except, probably, Te Aroha gas. Microbial reduction is a significant source mechanism for some of these methane gases. Thermogenic gases derived from the moderate (100-

150°C) heating of *sedimentary* organic matter, is the source of the methane of the others. Microbial oxidation affects methane by removal of the isotopically lighter molecules, preferentially moving the composition as shown by the arrow in Fig. 3. This usually minor secondary process has occurred in the fluids at Hot Water Beach and probably also at Okauia near Matamata.

The variations in methane $\delta^{13}C$ values are compared with the $\delta^{13}C$ variations in carbon dioxide in Fig. 4, and with the theoretical isotope equilibration temperatures. There are a wide range of values for carbon dioxide also. The most depleted values, from Okauia, *suggest* some addition of biological CO_2 from soils but most values are compatible with CO_2 extracted from sedimentary or volcanic rocks.

only some of these hot *springs* have indications of high temperatures. The gases from Te Aroha, Puriri, Hot Water Beach and Kaitoke Springs at *Great* Barrier Island have carbon-13 values indicative of equilibration temperatures >250°C (Fig. 4). Lyon and Hulston (1984) show however that *carbon isotope* temperatures are usually more than 100°C above measured geothermal field temperatures. The Okauia *springs* near Matamata, *the* Paeroa and Waitoa *springs* have carbon-13 equilibration temperatures less than 200°, and Kerepehi and Maketu have only microbial methane.

5. ACKNOWLEDGEMENTS

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