

STABLE ISOTOPE AND GEOCHEMICAL RECONNAISSANCE
OF THE MOKAI GEOTHERMAL SYSTEM, TAUPO VOLCANIC ZONE

J.R. Hulston*, R.W. Henley*, R.B. Glover* and M.A. Cox*

* Institute of Nuclear Sciences, Lower Hutt
+ Chemistry Division, Wairakei, N.Z.

ABSTRACT

Stable isotope and geochemical data from natural features at Mokai are consistent with a hot water upflow zone in the central area, and a shallow lateral flow with dilution towards the north-east. Chemical water and gas analyses indicate minimum temperatures of 200°C and 240°C , respectively. The hydrogen-water isotope temperatures are $\sim 290^{\circ}\text{C}$, while the methane-carbon dioxide isotopic temperature of 490°C ($\sim 100^{\circ}\text{C}$ higher than corresponding values in Wairakei or Broadlands), suggests a high temperature source at considerable depth in the central area. Oxygen-18 and deuterium analyses of thermal and ground-water support the proposed hydrologic model.

INTRODUCTION

The geology and hydrothermal activity of the Mokai geothermal system, 20 km north west of Wairakei, have been described by Lloyd (1978). Bibby (1977) described a preliminary geophysical survey, Dawson (unpubl) has completed a resistivity survey while Allis (unpubl) and Stagpoole and Grantham (in prep) have estimated natural heat flow.

Figure 1 shows the distribution of hot springs and fumaroles at Mokai. Gas-steam discharges are focussed north west and north of Mokai village associated with typical steam-heated features (mud pools, acid springs, shallow explosion or subsidence pits, etc). Warm ($56\text{--}58^{\circ}\text{C}$) dilute chloride springs occur only north of Mokai in the incised gorge of the Waipapa Stream at Mulberry Road and less mineralised warm waters are encountered in a shallow drillhole at the Tirohanga Maori Youth Camp (N84/420690). A number of warm seepages were known north west of Mokai on the south bank of the Waikato River prior to flooding for hydro electric storage.

GAS DATA

Six gas analyses are shown in Table 1. The gas composition of fumaroles are controlled by -

- (i) initial deep water composition,
- (ii) temperature of separation,

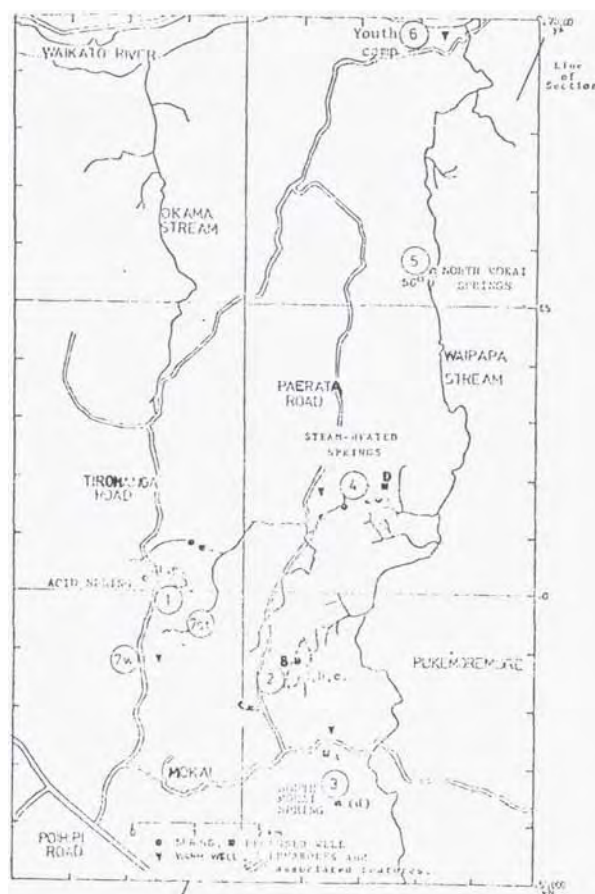


FIGURE 1. Distribution of hot springs and fumaroles in the Mokai area.

- (iii) amount of steam formed as a fraction of the deep water,
- (iv) whether steam is primary or secondary,
- (v) condensation.

Hulston et al.

The first formed steam contains the lowest CO_2/H_2 ratio, highest $\text{CO}_2/\text{H}_2\text{S}$ ratio and H_2/CH_4 ratio. As more steam forms these ratios change. If the steam flows through the country oxidation processes remove H_2S and condensation removes ammonia and increases gas concentrations.

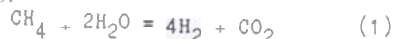
Using these criteria it is deduced that the gas supplying (3) has travelled a long way from its formation point i.e. little H_2S is present. Of samples (1) and (2), the latter appears to be closer to the deep water upflow zone than sample (1). i.e. the upflow zone is close to site B in fig. 1.

In order to estimate underground temperatures it is necessary to know the gas concentrations in the deep water. To calculate these we need to know the gas concentration in the steam and the steam fraction (i.e. iii. above). In table 1 we assume that firstly the steam collected represents 2% steam lost from the deep water and secondly that it represents steam formed by adiabatic steam separation to atmospheric pressure.

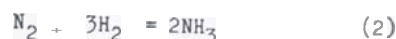
TABLE 1 - GAS ANALYSIS

Feature	Mokai West	Paerata Road	S.Mokai Bathhouse
Location	1	2	3
Date	12.77	12.77	12.77
Total Gas Composition mole %			
CO_2	88.88	91.48	99.75
H_2S	4.69	4.28	trace
H_2	0.522	0.70	0.0006
N_2	4.22	1.87	0.103
CH_4	1.63	1.52	0.150
NH_3	0.059	0.144	-
Gas Concentration (mm/100m Steam)			
CO_2	495	649	
H_2S	26.1	30.4	
NH_3	0.33	1.02	
Gas Ratios			
$\text{CO}_2/\text{H}_2\text{S}$	18.9	21.4	
CO_2/H_2	170	131	1.8×10^5
CO_2/CH_4	55	60	670
H_2/CH_4	0.32	0.46	0.004
Gas Temperatures ($^{\circ}\text{C}$)			
$\text{T}(\text{CH}_4.\text{O}_2)$	221	236	234
$\text{T}(\text{NH}_3.\text{O}_2)$	274	263	
$\text{T}(\text{CH}_4.\text{TA})$	301	316	
$\text{T}(\text{NH}_3.\text{TA})$	360	347	

Temperatures are then calculated from the following reactions:-



and



The temperatures calculated from reaction (1) are 211 to 236°C using 2% steam formation and 301 to 316°C using total steam formation. Thus a temperature of over 240°C is postulated.

The temperature from reaction (2) is much higher and more variable (263 to 303°C) for 2% steam. This is due to ammonia being very susceptible to removal near the surface which raises the calculated temperatures.

Giggenbach(1980) has suggested a gas geothermometer, based on a combination of the above reactions, which operates on the analysis of the gas fraction only (i.e. gas in steam concentrations are not needed). However this formula is heavily dependant on the ammonia component which as pointed out above is very variable in fumaroles and yields temperatures over 400°C with the data in Table 1.

Thus the temperature of 240°C is considered reasonable for initial steam separation from the deep water below proposed drill site B. As suggested by gas ratios and temperatures, the west Mokai fumaroles are located slightly further from the upflow portion of the geothermal system, than the Paerata Road activity.

GAS ISOTOPES

The gas isotope results (Table 2) show a remarkable similarity in the $\delta^{13}\text{C}$ values of CO_2 and CH_4 and in the δD values of CH_4 and H_2 between the samples from area 1 (West Mokai) and 2 (Paerata Road) thus pointing to a common origin for these gases. The isotopic temperature from $\Delta^{13}\text{C}(\text{CO}_2-\text{CH}_4)$ which is believed to represent temperatures at considerable depth (Hulston, 1977) is $485-490^{\circ}\text{C}$ for both these areas, while the $\Delta\text{D}(\text{H}_2-\text{H}_2\text{O})$ temperature which has a faster equilibrium time and usually indicates temperatures at drillable depth is indicated as 290°C for two samples. The equilibrium reaction mechanism between CH_4 and H_2O is still under investigation and the significance of the $\Delta\text{D}(\text{CH}_4-\text{H}_2\text{O})$ temperature is not certain at this time. Usually (Truesdell and Hulston, 1980 and Lyon and Hulston, 1980) $\Delta\text{D}(\text{CH}_4-\text{H}_2)$ and $\Delta\text{D}(\text{H}_2-\text{H}_2\text{O})$ temperatures are similar but the results in Table 2 suggest that $\Delta\text{D}(\text{CH}_4-\text{H}_2\text{O})$ represents temperatures closer to the surface than those derived from $\Delta\text{D}(\text{H}_2-\text{H}_2\text{O})$.

TABLE 2 - MOKAI GAS ISOTOPE ANALYSES

Location	Sample Date	Surface Temp $^{\circ}\text{C}$	$\delta^{13}\text{C}(\text{‰})$		$\delta\text{D}(\text{‰})$		Temperatures ($^{\circ}\text{C}$)		
			CO_2	CH_4	CH_4	H_2	$\Delta^{13}\text{C}$ CO_2-CH_4	AD $\text{H}_2-\text{H}_2\text{O}$	AD $\text{CH}_4-\text{H}_2\text{O}$
1. West Mokai	780217	99	-5.7	-20.25	-170	-438	490	285	140
2. Paerata Rd.	780217	99	-5.7	-20.4	-165	-434	485	290	170
3. South Wokai Bathhouse	780217	50	-3.9	-26.6	-201	-	320	-	45

The results from area 3 (South Wokai Bathhouse spring) give lower isotopic temperatures, indicating that this area is considerably distant from the main deep upflow region or is from a separate low temperature upflow.

These measurements thus suggest that the Mokai area has sufficiently high temperatures at depth to justify the drilling of exploration wells in the region. The isotopic results suggest that the best area for these wells would be in the region between the West Mokai fumarole (1 in Figure 1) and the Paerata Road mud volcano (2 in Figure 1).

WARM SPRING CHEMISTRY

Major element analytical data for the Mokai springs are shown in Table 3. Warm springs north of Mokai on the Waipapa Stream discharge near neutral pH dilute chloride waters at 56°C. Some 5 km further north the Tirohanga camp well encounters less mineralised 33°C water. A conclusive correlation of these two waters is not possible due to the significant analytical error involved for boron at low concentrations but Cl/B ratios of the two are similar. The southern Mokai spring (N93/417562) discharges a dilute sulphate bicarbonate water containing 39 ppm chloride together with gas, and probably represents a dilute steam-heated water (see gas analysis 3).

Table 3 gives water-source temperature estimates based on the now standard alkali ratio and silica geothermometric techniques (Fournier, 1977). Silica geothermometry is often equivocal in acid volcanic terrain, such as in the Taupo Volcanic Zone, where abundance of glassy or poorly recrystallised silica in the volcanic host rocks leads to silica concentration controls in natural discharges being determined by amorphous silica solubility (Henley and Stewart, 1981) or by the solubility of other silica phases such as chalcedony.

For the northern Wokai Spring, amorphous silica temperature estimates are less than spring outflow temperatures. Source temperature estimates by the Na Ca K geothermometer of Fournier and Truesdell (1973), corrected for dissolved magnesium (Fournier and Potter, 1979) are in the range 130-145°C. At these temperatures cooling fluids would not intersect the amorphous silica saturation curve, so that reliance can be placed on the quartz temperatures as indicative of source temperatures. These are somewhat higher (150-180°C) than the Na Ca K temperatures and due to dilution and reequilibration at lower temperature provide minimum estimates for the deep system.

WATER ISOTOPES

The $\delta^{18}\text{O}$ v δD relationship of these samples is shown in Figure 2. Three Mokai water samples (and one Atiamuri sample) show strong evaporative effects with δD enrichments of $>10\text{‰}$ and $\delta^{18}\text{O}$ enrichments of $>2\text{‰}$ relative to the majority of samples at $\delta^{18}\text{O} \sim -6.9\text{‰}$ $\delta\text{D} \sim -43\text{‰}$. In the main group of samples there is some indication of an $\delta^{18}\text{O}$ shift without a corresponding deuterium shift. If as suggested below the chloride springs are a mixture of local water and deep water of 1000 ppm then the 0.8‰ $\delta^{18}\text{O}$ shift for the 510 ppm chloride spring sample would suggest that the deep water had an oxygen-18 shift of 1.3 to 2.0‰. This has been indicated by the "Mokai Deep Water?" position on the graph. For comparison the inferred "Deep Wairakei" and "Deep Broadlands" values of Stewart (1978a, 1978b) have been shown in Figure 2.

TABLE 3 Spring water compositions & geothermometry, Mokai.

Sample	pH	Li	Na	K	CONCENTRATIONS						PPM		Total B	Total SiO ₂	As	Total HCO ₃	Spring temp °C	Geothermometer temp °C			Cl/B
					Rb	Cs	Ca	Mg	Cl	SO ₄	(a)	(b)						(c)			
North Mokai																					
L692	6.23	2.82	255	13.4	.146	.340	9.9	1.4	366	10	1	132	.5	229	59	32	103	131	113		
L693*	7.21		357	17.2			29.0	1.6	510	12	4	148		127	52	35	160	143			
L694	6.26		295	13.0			9.4	1.2	274	8	3	130		155	58	31	152	145	26		
L695	6.04	2.77	250	13.2	.142	.330	9.2	1.3	364	8	4	197		170	58	55	179	131	28		
L696	6.29		243	12.9			8.9	1.2	353	8	3	127		140	56	29	151	131	36		
L697	6.33		252	13.4			9.1	1.1	270	8	4	132		155	58	32	153	131			
Tirohanga Youth Camp Downhole Samples																					
L139/A	7.96		96	5.8			6.8	3.7	96	40		86				15	135	34	19		
L139/B	8.15	0.6	95	3.5	.021	.019	4.6	3.3	93	9	1	85				16	136	14	30		
South Mokai																					
L699	6.07		175	9.9			11.7	2.1	39	9		115		102	-	25	147	90			

* Low discharge pool.

Geothermometry. a) T_{SiO_2} for amorphous silica saturation and conductive heat loss.
 b) T_{SiO_2} for quartz saturation and conductive heat loss.
 c) T_{NaCaK} corrected for magnesium content.

Hulston et al.

The two steam condensate (fumarole) samples are depleted in both oxygen-18 and deuterium indicating steam-water fractionation effects. One method of estimating the temperature at which this equilibrium occurred is to assume that the water phase had an isotopic composition between that of local groundwater and the inferred deep water. Using $\delta D(\text{water}) \sim -43 \text{ ‰}$ and $\delta D(\text{steam}) \sim -56 \text{ ‰}$ yields an isotopic equilibrium temperature of 150°C (Friedman and O'Neil, 1977). At this temperature with $\delta^{18}\text{O}(\text{steam}) = -10.1 \text{ ‰}$ the equilibrium water phase has $\delta^{18}\text{O} = -6.7 \text{ ‰}$. Thus this simplistic approach suggests that the isotopic composition of the source water for these fumaroles is similar to that of the N. Mokai medium chloride warm springs (RWH4694-7). These results are thus in agreement with the suggestion below that the N. Mokai Springs arise from the Central and West Mokai area due to hydrostatic pressure from the slope of the land.

The springs from the site D region were labelled "steam heated springs" in Figure 1 because of their very low chloride content. The two lower temperature samples show no shift from the meteoric water line but there is a small positive $\delta^{18}\text{O}$ shift for the two 58°C springs.

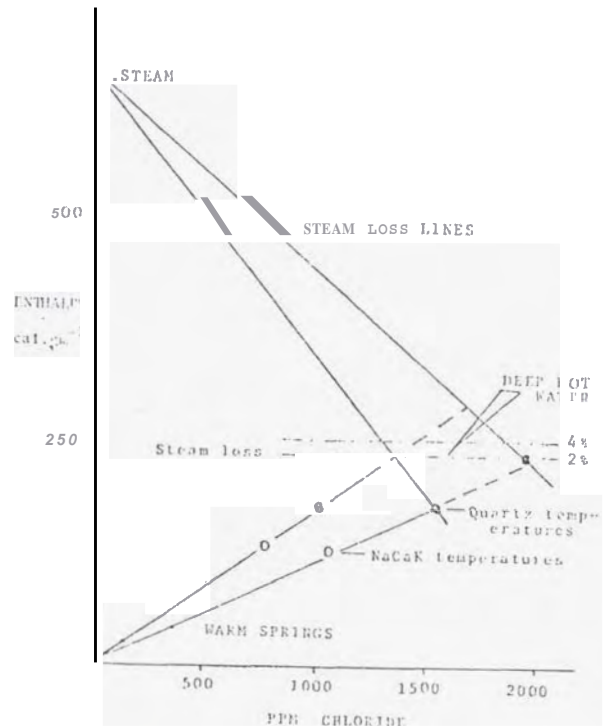


FIGURE 5. Enthalpy-chloride mixing model for warm springs and fumaroles at Mokai

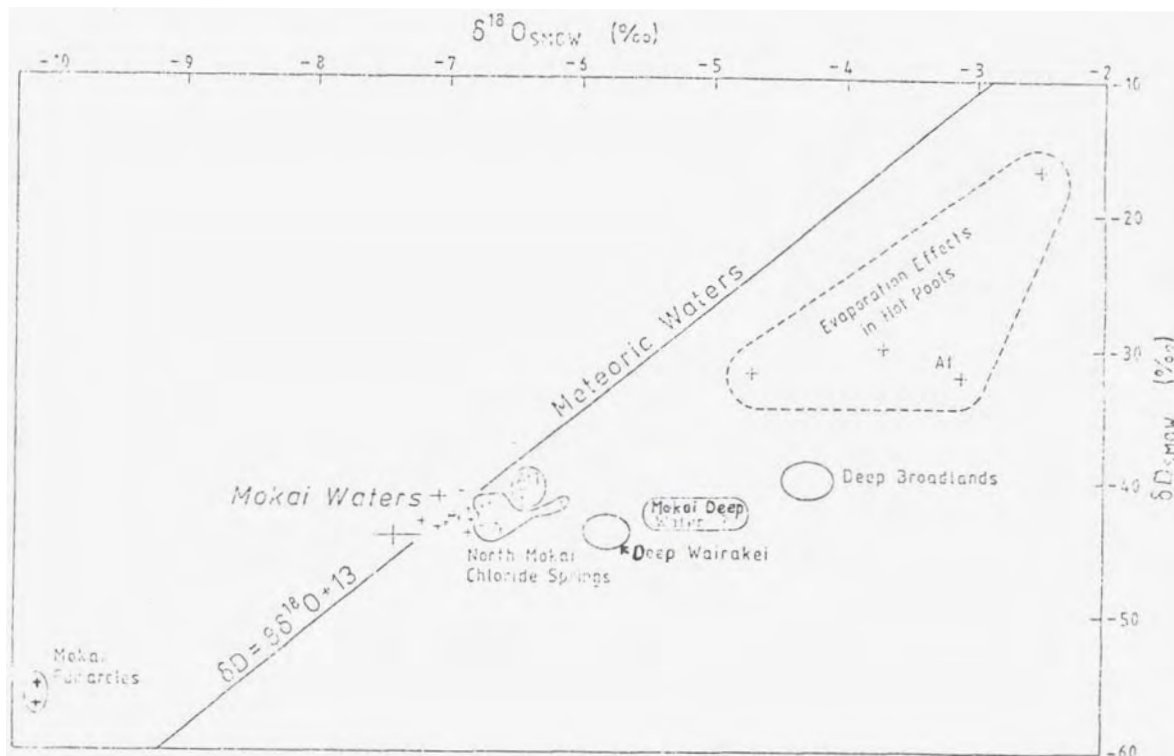


Figure 2. Mokai - Atiamuri Area.

Since a relatively small proportion of steam would be required to produce this temperature rise, the isotopic composition of the steam is unlikely to have altered the isotopic composition of these springs.

HYDROLOGY OF THE MOKAI SYSTEM

Healy and Hochstein (1973) have shown that in a number of geothermal systems, natural discharge of near-neutral pH dilute chloride waters may occur some considerable distance from the high temperature upflow portion of the parent system. For El Tatio in Chile and Okoy, S. Negros these distances are of the order 15 km. The actual distribution of springs reflects the local hydrological pattern.

The only chloride water discharges occur 8 km north-east of and at an elevation 250 metres lower than the major fumarole activity at Mokai. Both Lloyd (1978) and Allis (1980) have suggested that the regional hydrology and the unpublished resistivity data at Mokai suggest a lateral flow of chloride water north eastward across the Mokai caldera.

The acceptance of such a model allows a number of implications for exploration drilling and exploitation to be drawn from the available chemical data. The northern springs retain alkali ratios consistent with hot reservoir temperatures of 130-145°C.

Application of the wam springs mixing equations of Fournier and Truesdell (1974) suggests a 3:1 mixing ratio between cold groundwater and hot chloride waters on the basis of quartz-saturation control of silica contents and corrects the quartz temperatures for dilution to 185 - 200°C, and 2.5:1 to account for the alkali geothermometry. For these mixing ratios, chloride contents in the 120 to 175 portion of the system must fall in the range 750 to 1500 ppm chloride, depending upon the temperature assumed for cold water entering the flow system (Figure 3).

Gas temperatures (>240°C) are much higher than spring source temperatures. The minimum temperature difference between the two is too large to account for simply by steam loss so that some dilution must have occurred between steam loss and last water-rock equilibration at 130 - 145°C. Allowance for this additional dilution suggests deep water chloride contents in the range 1350-2000 ppm. Deep water chloride concentrations at Broadlands and Wairakei fall in the lower part of this range (1200 and 1600 ppm respectively).

The hydrological model adopted above implies that the thermal and chemical signature of the Mokai geothermal system is widely dispersed during northward flow through the groundwater system of the Mokai ring-structure. Thus the 10 MW heat flow due to the North Mokai springs and other recognisable natural features (Allis, unpubl, 1980) bears little relationship to the total heat flow from the system which, on the basis of chloride input to the Waikato River may be as high as 200 MW (Stagpoole and Grantham, in prep).

Figure 4 is a schematic section through a lateral flow system such as may occur at Mokai.

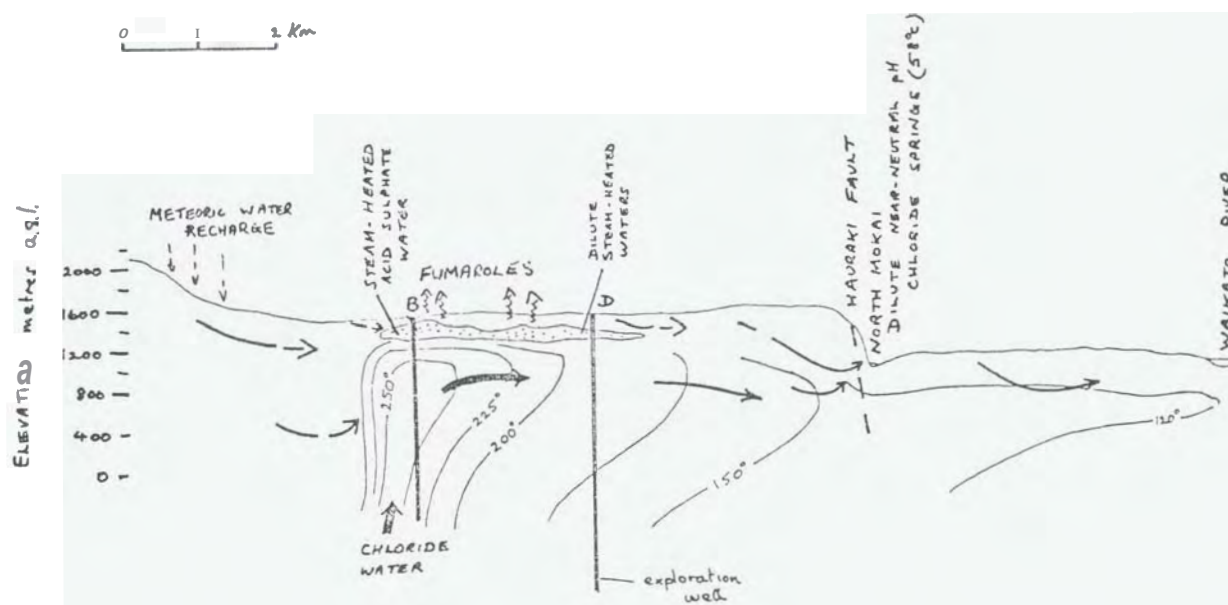


FIGURE 4. A SCHEMATIC LATERAL FLOW MODEL FOR THE MOKAI SYSTEM.

Hulston *et al.*

ACKNOWLEDGEMENTS

We thank Reiner Goguel, Lew Klyen (Chemistry Division), Graeme Lyon and Mike Stewart(INS) for assistance and advice.

REFERENCES

- Bibby, H.B. 1977: Preliminary geophysical survey of the Mokai geothermal area. DSIR Geophysics Division Geothermal Circular HMB1.
- Fournier, R.O., and Potter, R.W. II, 1979: A magnesium correction to the Na-K-Ca chemical geothermometer. *Geochim. et Cosmochim. Acta*, 43, 1543-50.
- Fournier, R.O., and Truesdell, A.H., 1973: an empirical Na-K-Ca geothermometer for natural waters. *Geochim. et Cosmochim. Acta*, 37, 1255-1275.
- Fournier, R.O., and Truesdell, A.H., 1974: Geochemical indicators of subsurface temperature - Part 2. *Jour. Research U.S. Geol. survey*, 2, 263-270.
- Friedman, I.; O'Neil, J.R. 1977: Compilation of stable isotope fractionation factors of geochemical interest. In M. Fleischer (editor) data of Geochemistry U.S. Geological Survey Professional Paper 440-KK; 12pp 49 figs.
- Giggenbach, W.F., 1980: Geothermal gas equilibria. *Geochim. et Cosmochim. Acta*, 44, 2021-2032.
- Henley, R.W., and Stewart, M.K., 1981: Chemical and isotopic changes in the hydrology of the Tauhara geothermal field due to exploitation at Wairakei. (in preparation)
- Healey, J., and Hochstein, M.P., 1973: Horizontal flow in hydrothermal systems. *Jour. Hydrology*, 12, 71-82.
- Hulston, J.R. 1977: Isotope work applied to geothermal systems at the Institute of Nuclear Sciences, New Zealand *Geothermics* 5 89-96.
- Lloyd, E.F., 1978: Preliminary report on the geology of Mokai geothermal prospect. DSIR N.Z. Geological Survey Geothermal Circular EFL-5.
- Lyon, G.L., Hulston, J.R. 1980: The significance of methane isotope geothermometers in some New Zealand geothermal areas. *Proceedings of the 4th International Symposium on Water-Rock Interaction*, Edmonton, Canada July 14 to 24 1980 pp 117-118.
- Stewart, M.K., 1978a: Stable isotopes in waters from the Wairakei geothermal area, New Zealand. In *Stable Isotopes in the Earth Sciences*, DSIR Bulletin 220, 113, 9.
- Stewart, M.K., 1978b: Isotope Measurements at Broadlands. INS Geothermal Circular MKS-2.
- Truesdell, A.H.; Hulston, J.R. 1980: Isotopic evidence on environments of geothermal systems. *Handbook of Environmental Isotopes Geochemistry Vol. 1*. P.Fritz and J-Ch Fontes (editors) pp 179-226.