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RECENT GEOCHEMICAL INVESTIGATIONS OF THE TOKAANU-WAIHI GEOTHERMAL FIELD

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Summary- The thermal source of discharges at both Tokaanu and Waihi have been reported as originating from a single coherent reservoir located at depth. New chemical and isotopic data were obtained to gain an understanding of processes such as mixing, dilution, boiling and cooling observed in these fluids. The geochemical interpretation of these processes shows that the primary upflow is towards the northwest boundary of the Tokaanu-Waihi field beneath an extensive area of *steaming* ground called **Hipaua**

1.0 INTRODUCTION

Chemical studies of thermal waters from the Tokaanu-Waihi area began with the early analyses of a few springs, published in 1882-1883 (20th Annual Report of the Dominion Laboratory; the analyses are *cited* in Robinson and Sheppard, 1986). Healy (1942) investigated the origin of boron in thermal waters at Tokaanu. This was the first comprehensive sampling and *chemical study* done at Tokaanu Healy suggested that the hot springs were associated with the escape of gases and *steam* from an underlying magma body, cooling at depth. This theory is *still* of interest since seismic swarm activity beneath Tokaanu-Waihi may be interpreted in terms of injection of molten rocks into deep basement fissures and dykes (Hochstein, et al., 1995).

Mahon and Klyen (1968), as part of a regional investigation of geothermal prospects in the TVZ, conducted a geochemical survey of hot springs at Waihi and Tokaanu to assess the extent of the geothexmal system and locate any undiscovered spring activity. The results suggested that the extent of the thermal area was confined to the zones outlined by Healy (1942) but did not exclude the possibility that the hot area extended into the lake, NE towards Motuoapa. As part of an inventory of geothermal resources and prospects, Hegan (1974) assumed that Tokaanu and Waihi were two separate geothermal *systems.* Robinson and Sheppard (1986) report chemical and isotopic data on water and steam samples collected m winter 1978 and autumn 1979 and infer the presence of a deep parent fluid of approx 250°C. They also *discussed* the hypothesis that the Tokaanu manifestations represent the end point of a long, concealed outflow of thermal waters, originating from a deeper brine Layer beneath the vapourdominated Ketetahi-Tongariro system, some 15 km to the west of Tokaanu.

Zhang and Wang (1987) and Sutaningsih (1994) studied geochemistry and hydrothermal alteration in the Tokaanu Domain. An investigation of the fluids and the extent of seepage at Waihi were carried out by Abdurahman (1994). The chloride flux of the Tokaanu Stream was studied by Reyes (1987) and recently resampled by Ha (1995). Seveme (1995) presented new chemical and fluid data, confirming a link between Tokaanu and Waihi but a distinct difference between these and the discharges on Tongariro. In Giggenbach (1996), further chemical and isotopic compositions of fluids showed consistent differences in the chemical and isotopic *analysis* of the composition of Tokaanu-Hipaua on one side, and vapors discharged from Ketetahi, Red Crater and Central Crater, on the other. The purpose of this present *study* is to provide chemical and isotopic evidence to delineate the mixing-boiling as the deep fluid ascends to the dace.

2. CHEMICAL COMPOSITION OF WATERS AND GASES

21 Sample Locations

Sample locations are shown in Figure 1, 13 features were selected for this *study.* The Waihi foreshore springs are all *close* to lake level, and their flow is controlled by the water level in the lake. When the lake is low the *springs* cease to discharge. The Tokaanu bores are less than 100m in depth and all were drilled in the early 1960s; the Oasis bore was redrilled in 1995. In the Tokaanu Domain one of the features is an investigation bore (Bore 2) drilled in 1942 (Healy 1942), it overflows continuously and an extensive sinter **apron** has formed. Other features in the Domain include Taumatapuhipuhi geyser and 2 overflowing boiling **springs.** **Two** of the gas **sampling** locations are situated within the *steaming* **ground** of Hipaua, the third is close to Bore 2 behind the **Tokaanu** Domain.

22 Water Compositions:

The chemical analyses of water samples collected at **Tokaanu** and Waihi are given in Table 1. Seventeen full sets of analyses per location have **been collected** but *only* 2 **sets** are **reported** in the present ***study.*** The **fluids** at Tokaanu are **characterised by high** Cl **and** Na **contents** of up to 3500 mg/kg and 1400 mg/kg respectively, these **values** were recorded in the Tokaanu Domain. The nearby **shallow bores** have **increasingly higher HCO,, Mg** and Ca concentrations, however the maximum value of these is found at in the **Waihi** foreshore springs. Increases in Mg, Ca **and** HCO_3 **concentrations** is typical of **waters** that have been diluted by **shallow** groundwater.

Relative Cl, SO, and HCO, contents of **fluids from** the Tokaanu-Waihi field have been plotted in **Figure** 2a. Unmixed **Tokaanu** samples **group at** the Cl apex of the plot.

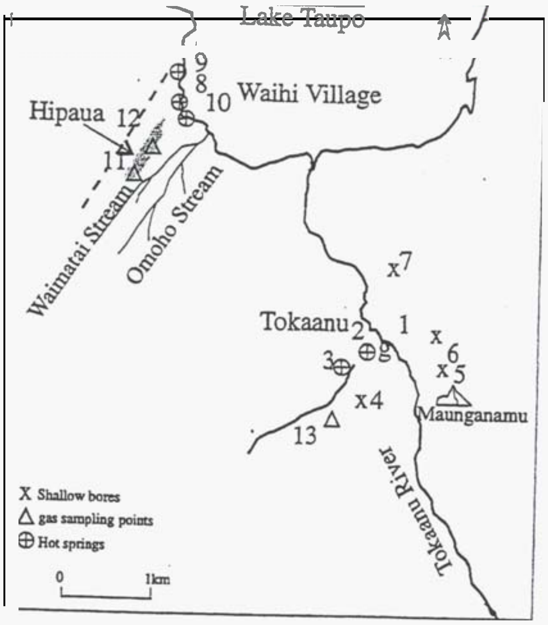

Figure 1: Sample locations

Sample	Date	Temp	pH	Li	Ca	Na	Mg	B	SiO_2	Fe	Cl	HCO_3	SO,	K
S1 Taumatapuhipuhi	5/3/97	100	8.2	21	37	1406	0.2	98	256	0.0	3155	30	61	170
	19/11/97	100	7.9	20	34	1292	0.2	13	234	0.1	3032	15	6	170
S2 Hoani	5/3/97	97	6.9	21	41	1395	0.7	101	320	0.0	3333	35	63	176
	19/11/97	98	6.9	20	37	1263	0.5	15	303	0.0	3140	31	63	175
S3 Toretiti	5/3/97	82	6.5	21	45	1361	0.4	104	315	0.0	3377	40	75	167
	19/11/97	80	6.4	18	36	1182	0.5	14	275	0.0	2913	6	73	155
S4 **Bore** 2	5/3/97	100	8	14	54	1022	1.6	67	294	0.0	2198	0	46	102
	19/11/97	100	7.9	12	48	913	1.5	10	258	0.1	2079	6	73	98
S5 **Rainbow** Hotel	5/3/97	75	7.8	7	52	703	14.2	32	241	0.2	1055	488	17	70
	19/11/97	70	7.6	7	47	642	13.6	6	234	0.2	1007	680	46	70
S6 **Oasis** Hotel	5/3/97	79	8.1	9	39	583	17.7	17	190	0.4	603	665	14	47
	19/11/97	78	8.1	5	37	497	18.7	18	207	0.3	576	351	17	47
S7 **Tokaanu** Hotel	5/3/97	76	7.3	9	57	509	37.3	20	206	0.0	727	331	8	48
	19/11/97	78	7.1	5	53	436	36.6	22	216	0.1	685	281	14	48
S8 Whakatara Bath	5/3/97	80	7	5	60	331	42.2	14	203	0.0	443	302	28	38
	19/11/97	68	6.8	3	52	286	37.9	14	199	0.1	425	306	8	39
S9 Te Tuki Bath	5/3/97	70	7.2	5	60	359	40.9	15	195	0.0	479	316	32	37
	19/11/97	70	6.6	3	57	280	44.3	15	207	0.0	433	150	28	34
S10 Whakatara Str	5/3/97	54	7.8	4	42	273	26.5	11	186	0.0	363	165	28	31
	19/11/97	56	6.9	2	39	222	26.3	4	199	0.0	317	183	27	28

Table 1: Chemical compositions of waters **discharging at** Tokaanu **and** Waihi, **all** concentrations in mg/kg.

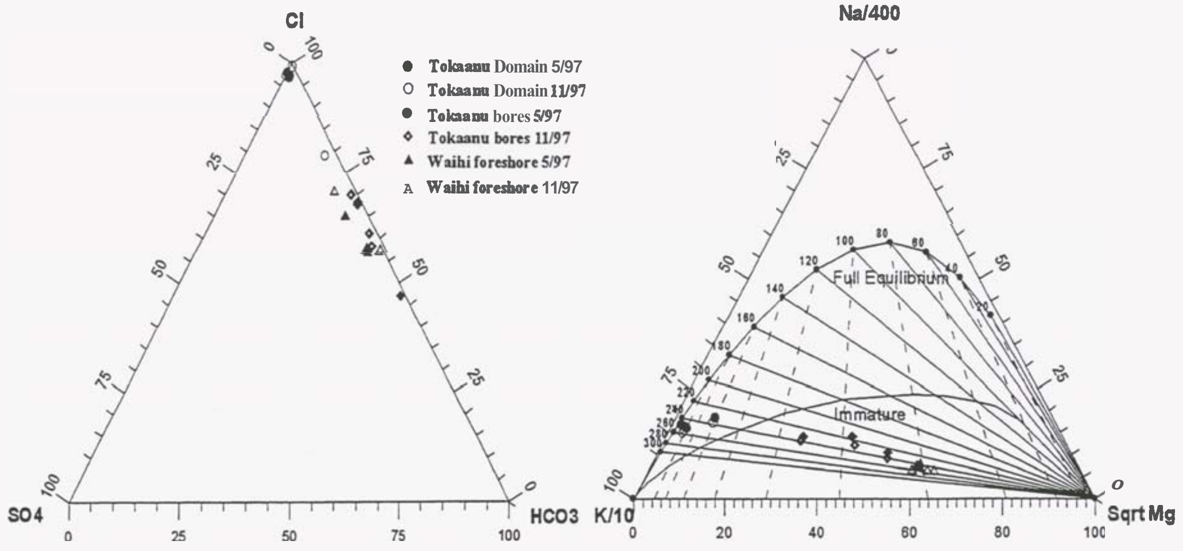

Figure 2: Plots of (a) relative Cl, SO_4 and HCO_3; (b) Relative Na, K, Mg contents of thermal waters of the Tokaanu-Waihi system (after Giggenbach, 1988).

Fluids found discharging at the Waihi Foreshore form the intermediate cluster of points midway along the Cl-HCO_3 axis; these are the 'mixed chloride-bicarbonate fluids, they also occur in several boreholes at Tokaanu The composition of these fluids is characterised by higher HCO_3 (mg/kg) values and correspondingly lower Cl (mg/kg) values.

The initial thermodynamic evaluation of the discharges uses the Na, K, and Mg contents of waters as shown in Figure 2b. Five of the samples fall on the full equilibrium line at 240-260°C. They are the samples with the highest chloride contents from the Tokaanu Domain, the least diluted by surface water and least affected by *steam* addition (highest Cl/SO_4 ratios). These waters also have the smallest HCO_3/Cl ratios; thus they are most likely to represent the deep parent fluid. A smaller portion of the samples from Tokaanu, plot in the sector with partially equilibrated fluids, this probably indicates some mixing and dilution at 200-220°C. The K-Mg subsystem responds faster than the Na-K *subsystem*, reflecting the greater speed with which the K-Mg geothermometer adjusts to a change in temperature (Giggenbach, 1988). The K-Mg temperatures reflect the conditions in the shallower parts of the system, and should be applied to the Waihi foreshore and Tokaanu bore waters, which are shifted in varying degrees towards the Mg corner away from the full equilibrium line and below the immature water line.

A diagram allowing the simultaneous evaluation of water-rock equilibrium for the geothermometers based on silica and K-Mg contents (Giggenbach et al., 1994) is shown in Figure 3. The two chemical systems represented in this diagram respond rapidly to the changes in temperature.

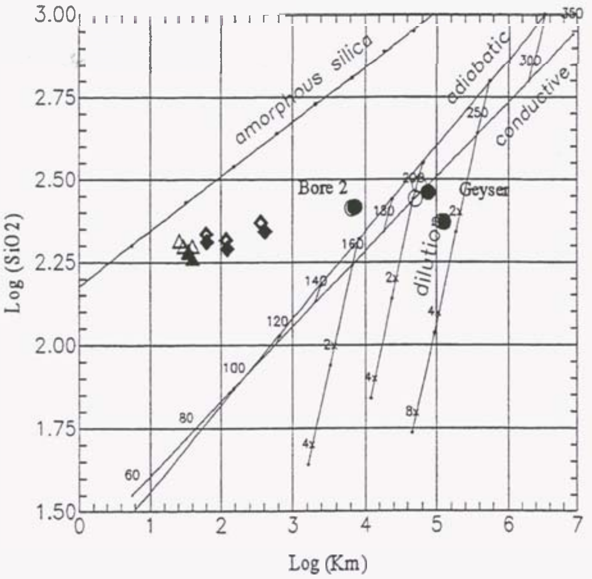

Figure 3: Evaluation of *silica* and K-Mg aqueous and fluid-mineral equilibria.

A cluster of data from the Tokaanu Domain plot on or near the *quartz* solubility line, the fluids have boiled before reaching the surface and therefore, their position should be on the adiabatic cooling line. Some fluids have obviously been diluted, however, the data indicates equilibrium temperatures between 160-220°C. As expected, the lower temperature HCO_3 springs in the Tokaanu Bores and at the Waihi Foreshore plot at considerably lower temperatures away from the quartz equilibrium line towards the line representing the control of silica contents by amorphous silica. In these features and Bore 2 from the Domain, the solubility of silica is controlled by more soluble polymorphs such as cristobalite or amorphous silica.

2.3 Chemical composition of gases

The chemical composition of steam discharges from Tokaanu and Hipaua are listed in Table 2; the Tokaanu Samples are the first uncontaminated analyses reported from this area. Apart from water, CO_2, H_2S and CH_4 represent the three major species in the samples listed in Table 2. The H_2S values (1-4 mmol/mol gas) are very low when compared with other fields in the TVZ, the lowest values occurring in the samples from Tokaanu Giggenbach (1996) suggested these low contents could be explained by the inherently low S content of the fluids from which the discharges of Tokaanu and Waihi originate.

Interpretation of the chemical composition of gases is difficult as samples collected from natural features at the surface are likely to have been affected by a variety of secondary processes, such as different degrees of vapour separation, condensation, mineral deposition, re-equilibrium, mixing and air contamination Due to these factors a technique involving the four species CO_2, CH_4, H_2, and Ar, based on concentration ratios devised by Giggenbach (1991), have been applied to the results. In Figure 4 ratios of H_2/Ar are plotted versus CO_2/Ar, the solid line marked "liquid" represents the compositions expected for attainment of equilibrium of the fluids with rock and with all gases dissolved in a single liquid phase (Giggenbach et al., 1994). Therefore, the position of the data points depends on the relative proportions of equilibrium liquid and vapour phases at the sampling point As gas is extracted from the fluid, its composition becomes closer to that of the deep equilibrium liquid phase and the data points plot close to the liquid line. All of the data points in Figure 4 plot below the liquid equilibrium line indicating that degassing or loss of vapour has occurred upstream of the sample points. Alternatively the position of the data points below the liquid line could reflect the readjustment of H_2 by re-equilibration at lower temperatures (200-260°C) (Allis et al. 1998). CO_2/Ar temperatures are higher between 250 and 300°C.

Sample	Date	He	H_2	N_2		Ar	H_2S	CO_2
Hipaua 1	19/05/97	0.01	0.60	11.3	25.6	0.04	4.6	957.9
	18/11/97	0.01	0.58	10.7	25.2	0.04	4.1	959.3
	18/11/97	0.00	0.58	8.5	20.7	0.03	4.8	965.4
Hipaua 2	19/05/97	0.00	0.56	7.1	17.0	0.03	3.3	972.0
	18/11/97	0.01	1.04	13.3	32.9	0.05	6.0	946.7
	18/11/97	0.0062	0.84	11.5	26.5	0.046	4.4	956.8
TK1	19/05/97	0.0026	0.34	11.2	32.1	0.05	1.8	954.5
	18/11/97	0.0049	0.24	17.8	42.1	0.097	0.9	938.8

Table 2: Composition of gas discharges from Tokaanu and Hipaua, all concentrations in mmol/mol gas.

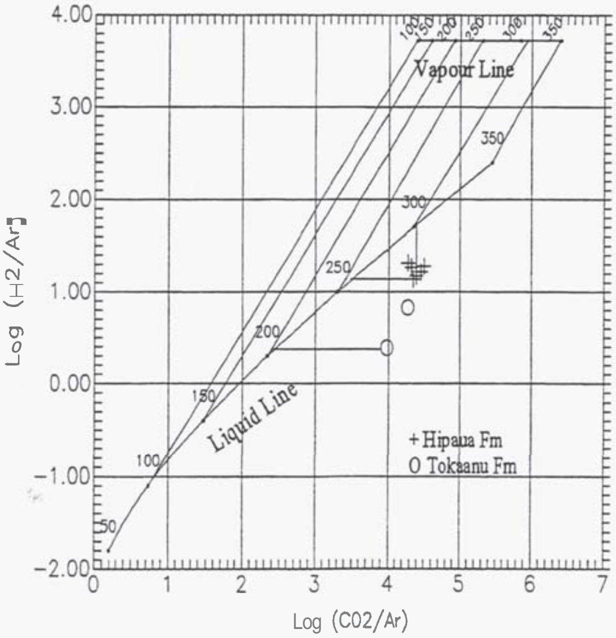

Figure 4: Evaluation of gas equilibration on the basis of H_2/Ar and CO_2/Ar ratios.

In figures 5 and 6 gas equilibria have been evaluated in terms of CO_2, CH_4, H_2 and Ar. In figure 5 the temperatures lie between the 250 and 300°C isotherms, the data has been affected by degassing but not to the same degree as in Figure 4. This confirms that the cooler temperatures reflect a combination of degassing and re-equilibration of H_2 in cooler conditions. Giggenbach (1987) found that reactions involving CH_4 were found to be slow and likely to reflect deep conditions, therefore, the suggestion of equilibrium temperatures close to 300°C could be possible. In Figure 6 there is little difference between the temperatures indicated by H_2/CH_4 and H_2/CO_2 geothemometers, which lie between 150 and 250°C. The points all lie well below the liquid equilibrium line. This can be explained again by a combination of degassing and re-equilibrium of the H_2 at lower temperatures.

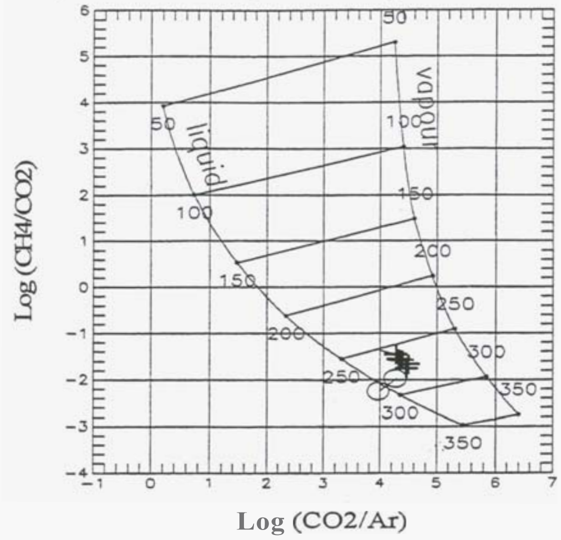

figure 5: Evaluation of gas equilibration temperatures on the basis of CH_4/CO_2 and CO_2/Ar ratios. Symbols are the same as those used in Figure 4.

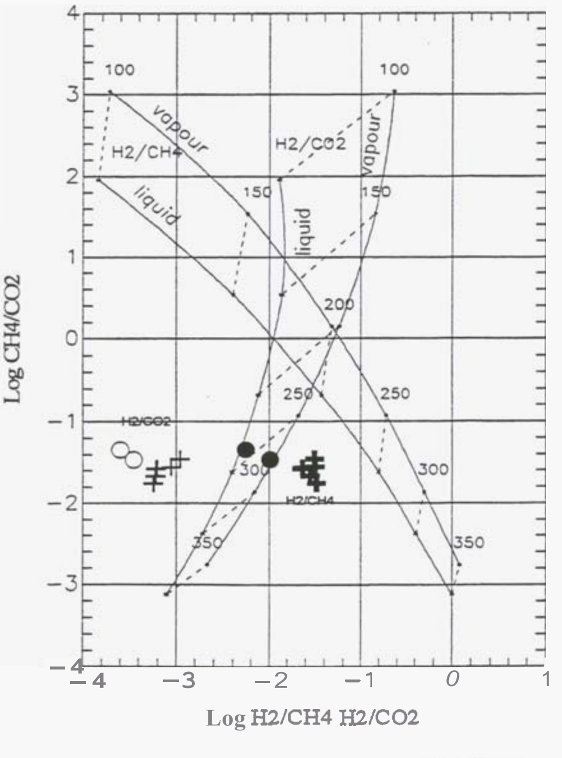

Figure 6: Evaluation of gas equilibration temperatures on the basis of CH_4/CO_2, H_2/CH_4 and H_2/CO_2 ratios. Symbols are the same as those used in Figure 4, in addition the *filled* in circles and bold crosses represent the symbols for the H_2/CH_4 ratio.

3.0 ISOTOPIC COMPOSITION OF WATERS AND CONDENSATES

In the previous sections we saw compositional evidence for subsurface mixing. It is now important to examine the stable isotope data to assess the effects of boiling and mixing of the deep fluid on its ascent to the *surface.* Robinson and Sheppard (1986) and Giggenbach (1996) discussed the isotopic compositions of waters discharged from the Tokaanu-Waihi area Their interpretation was based almost entirely on samples from the discharge waters, as they had *only* a total of 3 *steam* condensate samples. The stable isotope data from the present *study* has been given in Table 3 and shown in Figure 7. Cold meteoric waters in the area plot close to the average meteoric line for the area: $\delta D = 8 \times \delta^{18}O + 12$.

Date	No	$\delta^{18}O$	δD	Date	No	$\delta^{18}O$	δD
19/05/97	1	-2.6	-39.4	19/05/97	10	-5.3	-39
4/5/97		-2.7	-40.6	3/5/97		-5.9	-41
3/4/97		-2.7	-40.4	19/5/97	11 Hipaua 1	-6.7	-46
4/5/97	2	-1.2	-36.7	3/5/97		-6.5	-47
3/4/97		-1.0	-39.4	9/4/97		-7.7	-53
19/05/97	3	-0.3	-32.1	3/4/97		-6.9	-49
4/5/97		-0.2	-32	3/11/96		-8.2	-56
3/4/97		0.3	-33.4	1/11/96		-8.2	-57
19/05/97	4	-3.6	-38.2	27/10/96		-7.7	-52
4/5/97		-3.7	-37.9	9/4/97	12 Hipaua 2	-6.6	-46
19/05/97	5	-5.5	-38.6	3/4/97		-7.3	-51
4/5/97		-5.7	-43.2	3/11/96		-8.1	-55
3/4/97		-5.9	-41.5	1/11/96		-7.5	-51
19/05/97	6	-5.7	-40.6	30/10/96		-8.4	-57
4/5/97		-5.8	-40.3	27/10/96		-8.8	-59
3/4/97		-5.8	-42.3	19/05/97	13 Tokaanu	-11.6	-72
19/05/97	7	-5.9	-42	3/5/97		-12.2	-75
4/5/97		-5.8	-42.8	3/4/97		-12.9	-77
3/4/97		-5.9	-39.2	3/11/96		-14.4	-80
19/05/97	8	-6.0	-42.8	1/11/96		-14.0	-84
4/5/97		-6.0	-40.8	30/10/97		-10.1	-62
3/4/97		-6.1	-41.7	1979	Tokaanu R	-6.9	-40
19/05/97	9	-5.9	-41	1979	Tokaanu St	-7.2	-41
3/5/97		-5.8	-41.6	1979	Omoho St	-7.4	-42
3/4/97		-5.8	-42	1979	Lake Taupo	-5.8	-37
				1975	Lake Taupo	-5.3	-32
				1975	Waihi St	-7.1	-39

Table 3: Isotopic composition of Tokaanu-Waihi waters and gas condensates. Samples 1-10 are water, 11-13 are condensate samples from fumaroles located in Figure 1.

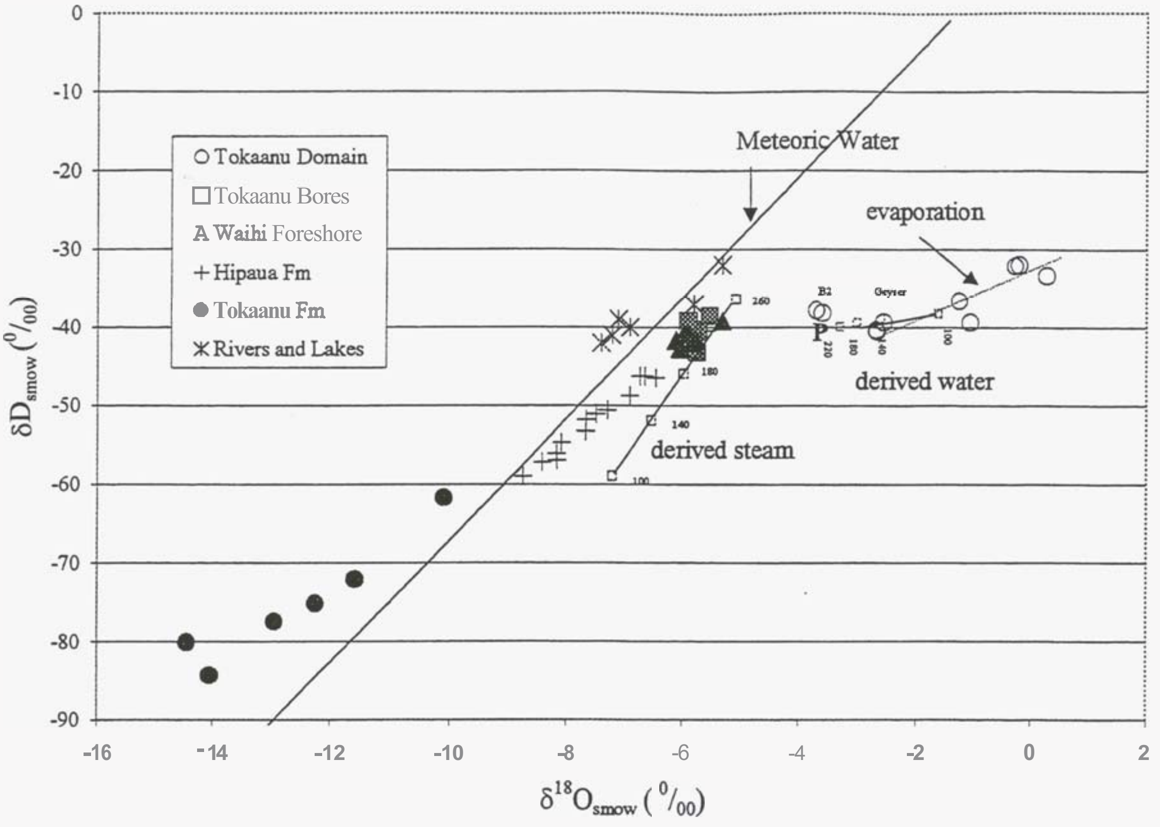

Figure 7: The isotopic compositions of water and *steam* discharges **from** Tokaanu and **Waihi, river** and lake **data has** been taken from Robinson and Sheppard (1986)

All of the samples except the Tokaanu *steam* condensate samples are enriched in δD and $\delta^{18}O$ which indicates there is enrichment by either evaporation, *steam* loss or oxygen isotope exchange of the hot water with the rocks or a combination of these. The data suggests that fluids discharging at Tokaanu derive from high chloride waters, with a *similar* composition to those supplied to the Taumatapuhipuhi geyser, Hoani and Bore 2 which are sample locations 1,2 and 4. The fluid from these locations is supplied from a deep parent water, which has a chloride content of close to 2300mg/kg chloride. The parent water has an initial isotopic composition P (Figure 7). The discharge fluid we observe at 1, 2 & 4 *may* be obtained by assuming maximum vapour loss of boiling from 260°C.

The Tokaanu fumarole samples have variable composition and the greatest depletion in δD and $\delta^{18}O$; these data lie to the left of the line formed from the *steam* derived from single stage boiling. As shown in Giggenbach and Stewart (1982), secondary steam generally lies to the left of the primary *steam* area in Figure 7. This effect is probably due to partial condensation loss of the liquid phase or the *steam may* be in part derived from heated ground water, this pattern was also observed at Tongariro Central Crater fumarole (Lyon & Stewart (1985). The Hipaua fumaroles appear to represent the *steam* derived from single *step steam* separation. These discharges have had little interaction with shallow environments and may have risen directly to the discharge points.

The samples with the most positive $\delta^{18}O$ values are Taumatapuhipuhi geyser and the pools 2 and 3, these samples also have exceptionally high chloride contents. This situation confirms Sheppard and Robinson's (1986) suggestions that evaporation or loss of *steam* has increased both Cl and stable isotope values by boiling. Waters affected by *surface* evaporation lie along a line on a slope of approximately 3 (Giggenbach and Stewart 1982). This type of non-equilibrium evaporation is evident in the Tokaanu Domain springs 2&3.

4.0 CONCLUSIONS

A combination of boiling and mixing of the deep reservoir fluids best explains the variation of the fluids discharging at different locations within the Tokaanu-Waihi Geothermal Field Previous interpretations of chemical data in Seveme (1995) and Sheppard and Robinson (1986) reach similar conclusions. The parent fluid at Tokaanu has a chloride content of 2400mg/kg, and an isotopic composition of $\delta^{18}O= -3.6‰$ and $\delta D=-42‰$. Relative concentrations of conservative components of the water and gas discharges clearly indicate that the shallower parts of this system are occupied by at least two distinct fluids. These are the fluids discharging in the Tokaanu Domain which are undiluted, chloride waters concentrated by boiling and mixed bicarbonate chloride waters discharging from shallow bores at Tokaanu and along the Waihi foreshore. The agreement of the geoindicators based on the Na-K, K-Mg and silica contents suggest that the waters discharging in the Domain have risen rapidly and with little interaction with other waters. These discharges appear to come from deeper zones governed by temperatures from 240-260°C.

The gas-geoindicator based on H_2/Ar and CO_2/Ar ratios indicate that deep equilibration temperatures lie between 200-300°C. This is consistent with the gas equilibration temperatures based on CO_2, H_2, CH_4 and Ar, which suggest temperatures between 150 and 300°C. The lower temperature has been interpreted as being a result of degassing and or re-equilibration by H_2 to cooler conditions as the fluid reaches shallower parts in the system.

The gas and isotope data combined show that the primary upflow is beneath Hipaua. The deep fluids undergo boiling at approximately 190°C, and are represented in the discharges such as those at B2 and Taumatapuhipuhi geyser (1 & 4). The isotopic composition of the less mineralised fluids at the Waihi foreshore, in the Tokaanu Domain springs 2 & 3 and in the Tokaanu bores is explained by simple mixing between the two end members; this also explains their lower chloride concentrations. The Hipaua steam discharges have higher gas contents than those from Tokaanu The Tokaanu steam discharges therefore, must originate from an excessively degassed secondary fluid.

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