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ARE TOKAANU CHLORIDE WATERS THE OUTFLOW FROM KETETAHI OR HIPAUA?

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SUMMARY - Waters discharged at Takaanu-Waihi have the highest Cl (3500 mgkg) and B (100 mg/kg) contents of the Taupo Volcanic Zone. Very high B contents in waters and steam at Ketetahi suggest a possible link. Relative Na-K-Mg and Ca contents of Tokaanu waters correspond to attainment of water-rock equilibrium at about 230°C. Ketetahi, some 20 km S of Tokaanu, produces highly immature, steam-heated, essentially NH_4-SO_4 waters. The isotopic composition of Tokaanu waters is compatible with derivation from both Ketetahi and Hipaua, another area of intense fumarolic activity some 3 km to the W. At Ketetahi, the inferred B contents of deep waters, however, are much too high, while those at Hipaua are suitable to act as source waters for Tokaanu. Relative CO_2, H_2S, CH_4 contents, and higher hydrocarbons in Tokaanu and Hipaua vapors are very similar, but differ consistently from those of the Tongariro discharges. The close relation between Tokaanu and Hipaua is strongly supported by the isotopic compositions of CO_2, CH_4 and He. All three areas, Ketetahi, including Red and Central Crater, Tokaanu-Waihi, and Hipaua appear to be associated with arc-type, probably andesitic magmatism.

1. INTRODUCTION

It was the high, economically possibly valuable B contents of the waters which attracted the first detailed survey in 1940 of the hot springs and fumaroles at Tokaanu, Waihi and Hipaua (Healy, 1942). A more comprehensive chemical survey was carried out by Mahon and Klyen (1968) who concluded that the Tokaanu-Waihi waters are heated by an andesitic intrusion, that they are supplied from a single deep source and that Cl, B, NH_4, Li, Rb and Cs are extracted from the andesite roughly in proportions found in the spring waters. They suggest that a link may exist between Tokaanu-Waihi and Motuoapa, 8 km to the east of Tokaanu. Robinson and Sheppard (1986) report chemical and H, O, C and S isotopic data on water and steam samples collected in winter 1978 and autumn 1979 and confirm the earlier conclusion that all springs tap a single 250°C reservoir.

The first major surveys of springs and fumaroles of the Ketetahi area were carried out by Wilson (1960) during 1936 and 37. He suggested that thermal activity of the Ketetahi type is due to due to secondary steam rising from hot Cl water at moderate depth. Because of the absence of any Cl water discharges in the vicinity of Ketetahi, he felt compelled to assume that the activity at Ketetahi is fed directly by magmatic steam, but considered the fate of the magmatic Cl a problem to be solved. Johnstone (1979) described fumarole encrustations, largely NH_4- and Al-sulfates, and some aspects of the thermal alteration at Ketetahi. Another detailed chemical survey and mapping of the Ketetahi area were carried out by Moore and Brock (1981) from 1971 to 1974. They stated that the activity there has not changed significantly for the preceding 40 years. Lyon and Stewart (1985) provide an a preliminary account of chemical and isotopic data obtained within this project.

Geophysical studies by Hochstein and Bromley (1979) outlined the resistivity structure of the Tongariro Thermal System and identified two highly conducting layers: one correlated with a shallow, acid condensate, the other with a deeper hot brine. Detailed measurements by Hochstein (1985) suggested a total heat output from Ketetahi of 36 MW, of 20 MW from the Red Crater area, and 5 MW from Te Mari. Moore and Brock (1981) estimated the total heat discharge from Ketetahi to be some 100 to 130 MW.

On the basis of chemical and isotopic evidence, Seveme (1995) explains the distribution of Cl and HCO_3 waters at Tokaanu and Waihi in terms of mixing of deep Cl and shallow steam-heated waters or condensates forming within the Hipaua system. The major aim of the present study is to provide additional chemical and isotopic evidence for the presence or absence of links among the three major hydrothemal systems of Tokaanu, Ketetahi and Hipaua.

2. CHEMICAL AND ISOTOPIC COMPOSITION OF WATERS

2.1 Analyticai Results

The chemical and isotopic compositions of water samples collected from the Ketetahi, Tongariro, Hipaua and Tokaanu thermal areas are given in Table 1. Altogether some 60 samples were analysed, largely collected during two major surveys of the Tongariro system in March and September 1975. Table 1 reports data for the most highly mineralised pools in the Main and East Basins of Ketetahi (KA to KD), and of features most likely to reflect changes in volcanic activity and of potential use in future geochemical monitoring programs, such as the outflows from the two main branches of the Ketetahi area (KM, KE), of water bodies occupying recent explosion craters, such as Blue Lake (BL) and the three Emerald Lakes (EL, EM, EU), and waters discharged at Soda Springs (SS) at the SW flanks of Tongariro. Apart from the Tokaanu waters, Cl contents in all the others waters were <5mg/kg.

Table 1. - Chemical (in mg/kg) and isotopic (in ‰) composition of water discharges from hydrothermal systems on Tongariro and at Hipaua and Tokaanu.

No	location	date	temp.	pH	Li	Na	K	Mg	Ca	B	Al	NH_4	SiO_2	Fe	SO_4	δ^2H	$\delta^{18}O$
	Ketetahi																
KM	Main Basin	7503	51	4.3	0.027	31	9.4	25.8	51	43	21	225	221	0.2	625	-29.4	+0.13
KM	Outflow	7509	48	3.3	0.033	31	8.9	32.2	67	23	67	220	220	1.3	630	-38.0	-3.24
KE	East Basin	7503	31	3.6	0.050	45	15.5	67.0	106	237	23	210	280	3.8	1475	-10.2	+5.65
KE	Outflow	7509	25	3.6	0.057	47	16.0	74.2	120	205	28	215	285	0.3	2960	-15.3	+4.63
KT	Total Outflow	7409	-	3.7	-	33	13.0	29.0	63	60	17	-	242	1.8	464		
KT	from	7503	25	3.5	0.030	32	10.1	29.0	57	53	28	120	231	0.8	705	-26.8	+0.95
KT	Ketetahi	7509	40	3.3	0.040	31	9.6	35.0	70	34	31	72	224	1.2	695	-40.7	-2.28
KB	Pools in	7503	96	7.4	0.004	16	6.4	10.5	25	30	<1	125	122	0.4	545	-19.6	+2.88
KD	Main Basin	7509	96	6.2	0.055	57	16.6	19.5	132	390	99	250	192	0.3	2025	-19.5	+4.15
KA	Pools in	7503	79	6.3	0.020	32	10.2	59.2	92	370	92	460	234	6.1	2625	-9.9	+8.50
KC	East Basin	7509	96	4.4	0.018	15	2.0	41.0	36	285	98	640	198	0.8	3810	-17.1	+5.14
	Tongariro																
BL	Blue Lake	7503	10	5.5	<.003	1	0.6	0.1	1	<1	<1	I	2	<.1	5	-39.5	-6.18
EL	Low Emerald L.	7503	8	4.3	<.003	2	1.0	1.7	3	<1	2	2	16	<.1	38	-52.8	-7.84
EM	Mid Emerald L.	7503	9	-3.4	< 003	2	1.2	1.7	3	<1	8	3	14	0.2	70	-39.2	-5.70
EU	Up. Emerald L.	7503	9	3.4	<.003	4	1.1	3.1	9	<1	20	1	23	0.2	130	-47.6	-6.72
SS	Soda Springs	7503	7	4.8	<.003	6	1.7	2.1	11	<1	I	I	55	0.1	45	-48.5	-8.21
	Hipaua																
HA	Boiling	79	94	7.4	<.1	27	9.0	6.6	18	<3	<1	3	136	-	92	-37.0	-4.60
HB	Pools	79	94	3.0	<.1	1	<1.0	1.8	1	9	10	2	189	-	570	-16.0	+0.80
	Tokaanu										HCO3	NH_4	Si02	Cl	SO4		
T1	Toretiti #IA	7610	85	7.2	4.8	378	36	4.2	42	22	240	6.4	213	596	28	-38.6	-5.03
T5	Domain #5	7610	70	6.4	26.0	1910	174	0.2	43	105	68	5.8	330	3219	76	-31.3	+0.62
T8	Well #8	7610	130	8.1	21.6	1596	136	0.2	43	82	62	3.2	221	2751	58	-40.3	-3.00
TW	Waihi	7610	96	8.2	3.5	302	'51	24.3	76	15	320	<.2	150	532	10	-40.0	-6.20

2.2 Chemical Composition of Waters

As stated already by Wilson (1960), the waters produced at Ketetahi contain NH_4 and SO4 as the major solute species, followed by silica and B. Chloride is with <5 mg/kg a very minor species. Their overall compositions are typical of waters formed above vapor-dominated systems by the absorption of vapors having separated from a deep brine into shallow groundwater. The high B content of the waters points to a high B content and, therefore, high temperature of the vapor. Such steam-heated waters provide only very limited information on deeper processes. In contrast, the waters discharged at Tokaanu contain high concentrations of Na and Cl, typical of "mature" waters and solute contents are likely to reflect closely conditions of water-rock interaction at depth.

On the basis of relative Cl, HCO_3 and B contents, Mahon and Klyen (1968) distinguish three distinct zones. Low HCO_3/Cl (<0.1) waters, as represented by samples T5 and T8, are discharged from the main Tokaanu thermal area. Waters discharged to the NE and NW, including Waihi (TW), have considerably higher relative HCO_3 contents. They are likely to reflect interaction of CO_2-charged waters with rock at low temperatures. The reduced Cl contents of the Cl-HCO_3 waters suggests that cooling is largely due to dilution with cool groundwater. The uniform HCO_3/Cl ratios, of about 0.6, indicate that the HCO_3 formed through interaction of the cooled CO_2-containing waters with rock before the onset of boiling, rather than interaction of waters heated by the absorption of steam. In the latter case, HCO_3/Cl ratios would be much more variable. Highly uniform B/Cl ratios of all the waters discharged at Tokaanu and Waihi (Mahon and Klyen, 1968) suggest that they are closely related and that they are only little affected by secondary vapor-separation processes.

Deeper water-rock equilibration temperatures and correlations among the various types of waters are evaluated in Fig. 1 on the basis of relative Na-K and Mg-Ca contents (Giggenbach, 1988). The Ketetahi waters plot to the left of the point marked "rock" indicating close to isochemical dissolution of an average crustal rock, followed by minor incorporation of K into secondary minerals, such as clays or alunite. The Tokaanu waters have highly variable Mg-Ca ratios at close to uniform K/Na ratios. The highest Cl samples (T5, T8) plot on the full equilibrium line at temperatures of about 230°C. The pattern of the data points in Fig. 1 suggests mixing of highly equilibrated, 230°C waters (T5, T8) with immature, Kdepleted, HCO_3 waters as represented by T1 and TW. In the case of mixing with waters resulting from direct rock dissolution, trajectories should follow one of the dashed mixing lines.

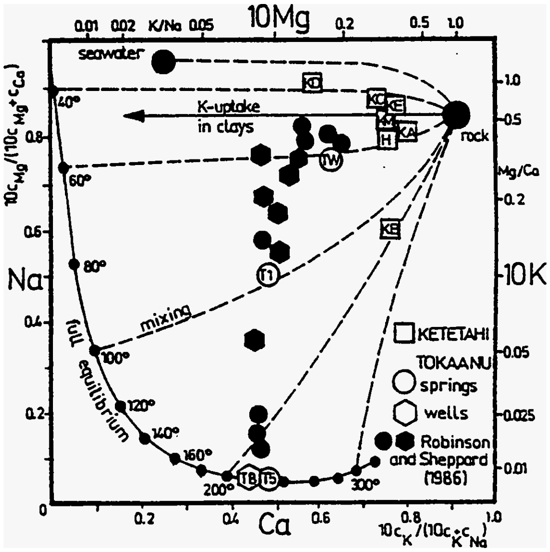

Figure 1- Relative Na-K and Mg-Ca contents of waters from Ketetahi and Tokaanu springs and wells.

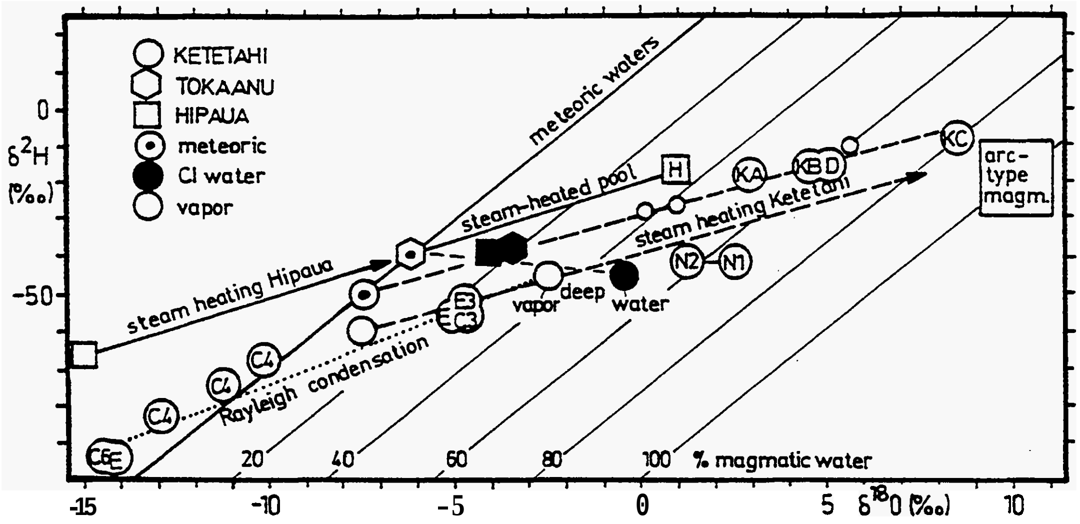

Figure 2- The isotopic compositions of water and steam discharges from Tongariro, Hipaua and Tokaanu thermal systems.

Summing up, waters produced at Ketetahi are formed through absorption of comparatively high temperature vapors, able to transport B, into shallow or surface waters. The waters discharged over the Tokaanu-Waihi area represent mixtures of a deep Cl water having equilibrated at about 230°C with Cl-HCO_3 waters resulting from the interaction of these same waters with rock at lower temperatures following dilution with cooler groundwater.

2 3 Isotopic Composition of Waters and Condensates

The isotopic compositions of waters discharged from the Tokaanu area were discussed by Robinson and Sheppard (1986), that of Ketetahi waters and steam condensates by Lyon and Stewart (1985). Their findings are summarised and discussed further in Fig. 2. By assuming the enrichment in the isotopic composition of the Tokaanu thermal waters to be due to interaction of local meteoric water with rock at elevated temperatures, Robinson and Sheppard (1986) derived values of -40‰ for δ^2H and -6.2% for δ^{18}O of the deep parent water, at a Cl content of 2500 mg/kg. Assuming the isotopic enrichment to be due to mixing with arc-type magmatic water (Giggenbach, 1992a), slightly higher 6^2H values of about -38% are obtained (solid hexagon). The isotopic compositions of parent waters underlying the Ketetahi and Hipaua vapor systems may be be evaluated by use of techniques reported by Giggenbach and Stewart (1982).

As already discussed by Lyon and Stewart (1985), the isotopic compositions of water discharges from Ketetahi springs and pools lie along a line with a slope of 2.65, typical of waters heated by the absorption of deeper vapors into local groundwater. This line intersect the meteoric water line at δ^2H of about -50‰ and 6^{18}O of -7.5‰ (Fig. 2). The isotopic composition of the steam heating these pools is represented by a line parallel to the steam-heated line and passing through a point representing the minimum isotopic composition, s,min, 50‰ lighter in ^{2}H and 16‰ lighter in ^{18}O than the most enriched pool (Giggenbach and Stweart, 1982). In case no data are available on the isotopic composition of this vapor, its ^{2}H content may be assumed to correspond to that of local meteoric water. At Ketetahi, however, isotopic data on steam comdensates are available, as listed in Table 3.

Isotopic compositions of steam condensates from the various features vary widely, especially those from the very low discharge Central Cratervent. Based on the differences in the composition of three samples (C4) taken consecutively in April 76, the most likely cause of this variability are Rayleigh-type condensation processes m the sampling tram, as indicated by the dotted line. Similar condensation processes may affect the vapors during their rise to shallow levels and may be responsible for some variability, such as the depletion in heavier isotopes in samples from the vent in the East Basin (E2 to E4).

Data points for Red Crater and the high-pressure vent (M1 to M8) in the Main Basin of Ketetahi occupy a comparatively narrow range corresponding to a mean of $\delta^2H = -47 \pm 4‰$ and $\delta^{18}O = -2.6 \pm 0.4‰$, right on the line marked "steam heating Ketetahi". It also falls close to the line linking Ketetahi local meteoric water (-50‰, -7.5‰) to "arc-type magmatic" water (-20‰, +10‰). Assuming the Ketetahi system to have attained steady-state with respect to the supply and discharge of magmatic and meteoric water, the composition of the vapor corresponds to the presence of about 32% of magmatic water. Also assuming vapor-liquid interaction processes within the vapor-dominated zones of the Ketetahi system to take place at the temperature of maximum enthalpy steam (236°C), as observed at other vapor-dominated systems (White et al., 1971), the isotopic composition of any coexisting iiquid would be heavier m δ^{18}O by about 2‰ and lie at the point marked "deep water". A line connecting the composition of the deep water at Ketetahi, with the point representing Tokaanu meteoric water (TM), passes close to the composition of the deep supply inferred for Tokaanu, a finding compatible with the assumption that Tokaanu waters may represent the outflow of deep Cl waters from the Ketetahi system. In this case, the Tokaanu waters would contain about 45% of deep Ketetahi, or 19% of magmatic water.

Another system possibly supplying Tokaanu with Cl waters is that associated with the Hipaua steam field, some 3 km to the **W.** Information **on** the isotopic composition of steam-heated waters there is very limited. Robinson and Sheppard report values of $\delta^2H = -16‰$ and $\delta^{18}O = +0.8‰$. Assuming groundwater at Hipaua to have a composition close to that at Tokaanu, a line is defined, again allowing the derivation of a trend line marked "steam heating Hipaua". Because of the somewhat steeper slope of the line "Hipaua stem-heated pool", the "steam-heating" line passes through the composition **of** Tokaanu meteoric water. Assuming the ^2H content of the Hipaua vapor to correspond to that of the local meteoric water, the composition of the associated liquid plots close to that of the Tokaanu deep water, suggesting that, **on** the basis of isotopic evidence alone, both Hipaua and Ketetahi could supply the waters feeding the Cl **springs** at Tokaanu. In addition to the isotopic species, the distribution of suitable chemical species, such **as** S, NH_3 and B, between vapor and liquid may provide additional evidence **as** to the relationship of Hipaua and Ketetahi vapors with Tokaanu waters.

2.4 Vapor-liquid distribution of S, NH_3 and B

In contrast to the little soluble species, such **as** CO_2, CH_4, H_2, N_2 and the noble gases, S, NH_3 and B, while comparatively volatile, they have also a tendency to be absorbed into shallow waters. Giggenbach and Stewart (1982) proposed a procedure **allowing** the concentrations **of** these species in steam-heated pools to be related to those in the parent vapor. It assumes complete absorption and is based **on** the relation

$$X_i = c_i(\Delta_{pw} - \Delta_{sh} + 14)/(56MW_i\Delta_{sh}) \tag{1}$$

where X_i is the mole-fraction of the species i in the vapor, in mmol/mol, and c_i the concentration of the species i, in mg/kg, in the pool waters. Δ_{pw} is the difference in the $\delta^{18}O$ values of the supply steam, and Δ_{sh} the measured increase in $\delta^{18}0$-values in steam-heated pools with respect to local meteoric water (-7.5%~). MW_i is the molecular weight of the species dissolved in the liquid phase (96 for SO_4, 17 for NH_3, 10.8 for B),

In **Fig.** 3A, dissolved SO, contents of Ketetahi steam-heated waters are plotted versus their $\delta^{18}O$ isotopic compositions, together with trend lines calculated by use of eqn (1) **as** a function of X_{H_2S}. From the data reported in Table **2**, the mole-fractions of H_2S correspond to

$$X_{H_2S} = x_g x_{H_2S}/1000 \tag{2}$$

and are in the main vent 1.8±0.7 mmol/mol. Comparison of theoretical and observed values shows that data points lie well below the 2 mmol/mol curve. The **most** likely explanation for the low SO, values is incomplete absorption, or conversion of H_2S to SO_4, in the pools, allowing much of the fumarolic H_2S to escape to the atmosphere.

A much more soluble species, especially in waters made acid **by** the oxidation of H_2S, is NH_3. **Its** behavior is illustrated in Fig. **3B.** According to Table 1, NH_3 contents in steam of the Ketetahi main vent are 0.2020.04 mmol/mol, values corresponding closely to those expected theoretically. The B contents of the steam-heated **pools** suggest B contents of the parent vapor of the order of 0.1 to **0.5** mmol/mol, a range overlapping **with** the **B** contents of 0.15 and 0.08 mmol/mol of the **two** steam condensates M2 and **M4** **as** listed in Table 2. Accepting a B concentration of about 0.25 **mmolimol,** or 150 mg/kg, the B concentration in the brine possibly underlying Ketetahi may be evaluated **by use** of the B vapor-liquid distribution coefficients $B_B = c_{B,v}/c_{B,l}$ **as** reported by Glover (1988). Their temperature dependence corresponds to

$$\log B_B = 0.00669t - 3.0506 \tag{3}$$

and B concentrations in a deep water of 200°C become 7900 mg/kg or 3600 mg/kg at 250°C. Such a water diluted to 45%, **as** indicated **by** the isotopic composition of Ketetahi and Tokaanu waters, would contain 1600 to 3500 mg/kg, values far above the maximum value of 105 mg/kg given in Table 1. **As** there are no secondary reactions allowing large **amounts** of B to be removed, it appears unlikely that Tokaanu waters represent the outflow of Cl water from Ketetahi. Nevertheless, assuming the B/Cl ratio of the Ketetahi deep water to be similar to that of the Tokaanu waters of about **0.03**, its Cl content would be 53 000 to 117 000 mg/kg. The only evidence for the occurrence of such highly concentrated brines beneath Ketetahi are the high, deep electrical conductivities observed by Hochstem and Bromley (1979).

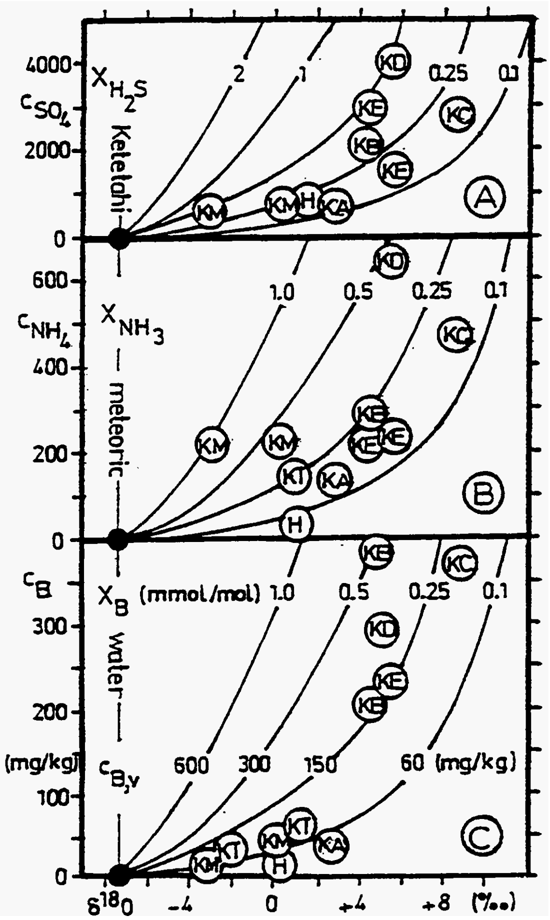

Figure 3 - Variations in SO_4 **(A)**, **NH_3** **(B)** and **B** (C) contents of Ketetahi waters (in mg/kg) **as** a function **of** their ^{18}O isotopic composition, in **‰.** Curves were calculated **by use** of eqn (1), **as** a function of X_i, **in** mmol/mol. For symbols see Table 1.

Table 2. Chemical compositions of vapor discharges from Tongariro, Hipaua and Tokaanu thermal systems, in mmol/mol of dry gas. x_g is the fraction of gas in the vapor, also in mmol/mol.

No	date	t(°C)	x_g	CO_2	H_2S	NH_3	B	He	H_2	Ar	O_2	N_2	$N_{2,exc.}$	CH_4	C_2H_6	C_3H_8	C_6H_6
Ngauruhoe																	
N1	780701	520	40	401	425	0.1	-	.0118	66	0.210	1.00	42.4	30.4	.007	-	-	-
N2	790224	516	101	696	179	0.1	-	.0044	28	0.549	2.00	62.4	32.0	.002	-	-	-
Red Crater																	
R1	730909	95	26	931	31	4.1			5			9.1		21	-	-	-
R2	740922	95	29	950	28	-			3			6.2		20	-	-	-
R3	750901	95	31	925	32	-	0.2	-	4	0.011	-	8.5	8.0	21	-	-	-
R4	760417	95	35	916	33	3.1	0.6	-	4	0.017	<.01	25.1	24.3	19			
R6	790224	98	35	950	17	1.9	-	.0027	4	0.014	0.02	8.5	7.8	19	,0016	,00013	.0004
R8	830504	95	43	949	24	1.7	-	.0048	3	0.020	<.01	7.2	6.2	16	.0016	.00014	.0009
R9	880214	94	42	935	23	4.2	-	.0011	4	0.110	0.02	11.5	6.0	23	.0051	.00039	,0009
Central Crater																	
C2	740922	95	84	956	19	-			3	0.011	-	8.8	8.3	13	-	-	-
C3	750901	95	48	945	22	-			2	0.011	-	8.8	8.3	22	-	-	-
C4	760417	95	77	950	20	0.1	0.1	-	4	0.013	<.01	7.2	6.6	19			
C6	790224	87	66	918	33	0.1			4	0.135	0.01	23.2	16.5	21	.0019	.00025	.0003
C8	830504	74	75	972	2	c.1	-	.0036	2	0.010	<.01	8.0	7.5	17	.0017	.00017	.0003
Main vent																	
MO	5604--	-	30	925	26	-			20			9.8		20	-	-	-
M1	730909	132	72	896	32	3.0			29		-	14.3		26	-	-	-
M2	740921	132	50	938	31	2.4	3.0	-	11		-	20.6		38	-	-	-
M4	760417	138	64	896	34	2.4	1.3	-	25	<.010	<.01	12.0		30	-	-	-
M5	771207	134	80	901	31	2.3	-	.0023	28	0.020	<.01	11.6	10.6	27	-	-	-
M6	790225	136	31	884	44	5.3	-	.0076	26	0.012	0.02	13.9	13.3	27	.0019	.00019	.0003
M7	790914	136	64	904	30	3.9	-	.0040	23	0.010	0.01	13.3	12.8	26	.0029	.00023	.0011
M8	830504	119	37	826	21	-	-	.0040	17	0.020	<.01	9.5	8.5	16	.0017	.00013	.0002
M9	880214	102	58	910	27	4.0	-	.0040	20	0.007	<.02	14.0	13.7	24	.0065	.00050	.0009
Eastern Vent																	
E2	740921	118	89	904	30	-			23		-	23.0		20	-	-	-
E3	750901	128	104	895	32	-	0.2	-	25	0.010	-	14.5	14.0	34	-	-	-
E4	760417	-	88	810	33	2.1	0.3	-	22	0.780	<.01	107.0	68.0	25	-	-	-
E5	771207	120	46	892	32	3.8	-	.0035	29	0.047	<.01	15.5	13.2	28	-	-	-
E6	790224	98	142	914	22	1.0	-	,0050	24	0.013	0.02	12.9	12.3	26	.0023	.00018	.0005
E8	830504	122	57	900	26	3.9	-	.0049	22	0.020	<.01	10.1	9.1	18	.0019	.00014	.0003
Hipaua																	
H1	940914	91	37	941	4.0	1.1	-	.0073	.6	0.067	<.02	16.5	13.2	36	.0223	.00130	.0144
Tokaanu																	
T	790225	96	-	860	1.4	0.01	-	.0049	.4	1.420	16.3	103.3	7.5	19	.0170	.00112	.0094
T	790225	73	-	861	2.2	0.02	-	.0037	.4	1.800	15.7	95.8		24	.0256	.00167	.0092
T	880106	97	-	490	<.3	0.05	-	.0030	.1	5.500	35.1	304.0		7	.0086	.00065	.0179

Applying eqn (1) to sample HB from Hipaua (H), the B content of the vapor is 0.02 mmol/mol or 12 mg/kg. This value is close to the range of B contents (12 to 42 mg/kg) reported by Healy (1942) for a number of steam condensates collected by S.H. Wilson at Hipaua in 1940. The B content of an associated 200°C water would be 600 mg/kg, or 270 mg/kg at 250C. Allowing for some dilution, these values are at least comparable with the values of up to 105 mg/kg in Tokaanu waters and would support the assumption that these waters represent the outflow of Cl waters from the Hipaua hydrothermal system.

3 CHEMICAL AND ISOTOPIC COMPOSITION OF GASES

3.1 Analytical Results

The chemical compositions of vapor discharges from the Ketetahi, Hipaua and Tokaanu thermal areas are listed in Table 2. Values of x_g are the fractions of gas in the vapors, values of x_i the fractions of individual gases in the "dry" gas, both in mmol/mol. Fractions X_i in the total discharge are obtained by use eqn (2). Concentrations c_i in total discharge, in mg/kg, correspond to

$$c_i = x_g x_i MW_i/MW_{H_2O} = MW_i x_g x_i/18 \qquad (4)$$

For N_2, two values are given. the first one as measured. the second. $N_{2,exc.}$, represents the excess above atmospheric N_2 obtained by first subtracting $3.73x_{O_2}$ from measured N_2 contents and $0.0446x_{O_2}$ from measured Ar contents to obtain $N_{2,corr.}$ and $Ar_{corr.}$, corrected for obvious air contamination, and then $50x_{Ar,corr.}$ from $N_{2,corr.}$.

3.2 Relative CO_2, H_2S and CH_4 Contents

Apart from water, CO_2, H_2S and CH_4 represent the three major species in the samples listed in Table 2. The contents of all three are likely to be affected by temperature- and redox-dependent equilibrium processes, and due to their different solubilities in liquid water, also by vapor-liquid separation processes (Giggenbach, 1980; 1992b). Rates of redoxdependent reactions are much faster for reaction participants dissolved in a liquid phase, faciliting interaction of fluid phase components with di- and tri-valent Fe of the rock. rather than for species in the vapor phase. In vapors extracted from full equilibrium. even vapordominated systems, relative volatile contents generally approach those expected for attainment of fluid-rock equilibrium in the liquid phase. This overall conclusion is confirmed by the position of data points in Fig. 4 for the Tongariro gases close to the 'liquid' equilibration line at temperatures of around 250°C. There appear to be no significant differences in the compositions among the three sub-areas, Ketetahi. and Central and Red Craters suggesting uniform equilibration conditions within the entire Tongariro system.

Again data points for Tokaanu and Hipaua occupy distinctly different positions. beyond the "vapor" equilibration line. at much lower relative H_2S contents. corresponding to apparently much higher temperatures.

Several processes may be invoked to explain the low H_2S contents. One, of course, is to accept the high temperatures indicated by Fig. 4 at face value and to assume equilibration in the vapor phase. This, however, is unlikely as other geothennometers, such as Fig. 1, the ^{18}O-sulfate-water geothexmometer (Robinson and Sheppard, 1986), and those involving H_2 and Ar (not shown) actually indicate comparatively low temperatures.

Accepting equilibration reactions within the Hipaua-Tokaanu system to occur at comparatively low temperatures (<250°C), the low H_2S contents may be due to interaction of the fluids with aerated groundwater. By use of the values given in Table 2 for x_g and x_{H_2S} and eqn (2), the concentration of SO_4 resulting from oxidation of the H_2S in an Hipaua vapor would be about 950 mg/kg, far above those of 60 to 80 mg/kg observed in Tokaanu waters. The most likely explanation is an inherently low S content of the fluids supplied to the Hipaua-Tokaanu hydrothermal system.

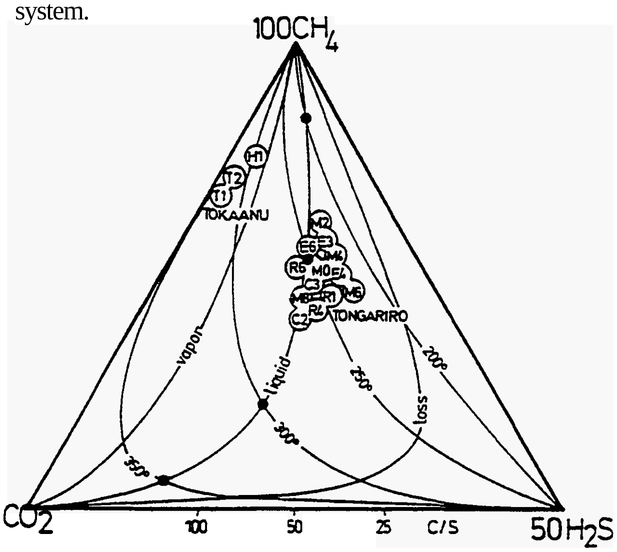

Figure 4- Relative CO_2, H_2S and CH_4 contents of Tongariro and Hipaua-Tokaanu vapor discharges.

3.3 Arc- versus Rift-type

The above findings suggest that Ketetahi and Hipaua-Tokaanu represent independent systems, likely to be supplied from different sources. Ketetahi, located on an andesitic volcanic structure is likely to belong to the group of "arc-type" hydrothermal systems as defined by Giggenbach (1995). Located on the margins of the Taupo caldera, a center of rhyolitic magmatism, Hipaua-Tokaanu-Waihi might well be a "rift-type" system. One of the most useful ways to discriminate among the two possibilities is based on relative excess N_2, He and C02 contents.

As shown in Fig. 5, the gas sample from Hipaua plots right among the Ketetahi gases in the region of the diagram typical of arc-type volatiles. Because of the high degree of contamination with air, only one sample from Tokaanu, T1, gave reasonable values of $N_{2,exc.}$. Its composition plots also close to the Ketetahi data. There appears to be a significant difference among the Tongariro gases with the Red and Central Crater samples plotting at somewhat lower, samples from Ngauruhoe at considerably higher excess N_2 contents. Ignoring these complications, relative N_2, He and C02 contents suggest that all three areas, Ketetahi, Hipaua and Tokaanu are associated with arc-type, or andesitic magmatism.

Additional support for this conclusion is provided by ethane/propane ratios which are with 10±2 for all samples quite uniform and close to those expected for arc-type systems (Giggenbach, 1995). Rift-type systems are characterised by lower ratios approaching those for natural gas of about 2.5.

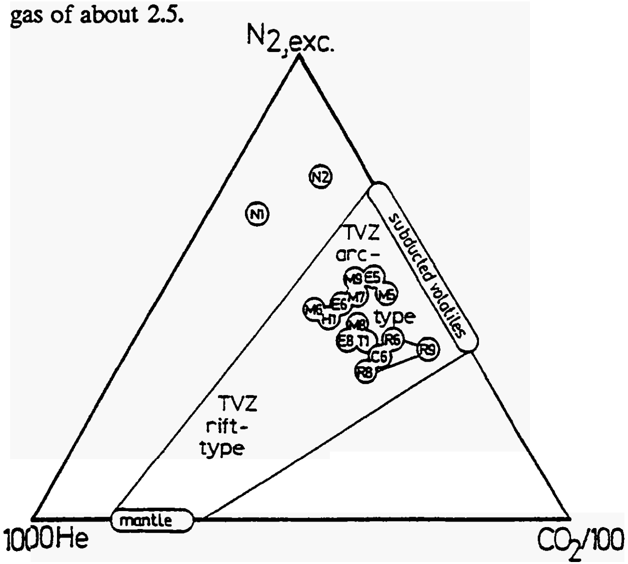

Figure 5 - Relative N_2, He and C02 contents of vapors discharged from Tongariro and Tokaanu-Hipaua thermal systems.

3.4 Isotopic Composition of Carbon, Sulfur and Helium

Additional information on the origin and evolution of hydrothermal fluid discharges is obtained from the isotopic compositions of C, in CO_2 and CH_4, and He, as listed in Table 3. The fractionation of ^{13}C between CO_2 and CH_4 is both temperature- and time-dependent (Giggenbach, 1982). Based on a recent re-evaluation of the kinetics of ^{13}C equilibration (Giggenbach, unpubl. res.), the half-time for the approach to isotopic equilibrium between C02 and CH_4 is about 100a at 400°C, 1ka at 300°C and 100ka at 200°C. Assuming migration of the volatiles from a high-temperature, magmatic environment to lower temperatures, these half-times provide a measure for the time the gases have resided underground before attaining the observed fractionation.

The distribution of data points in Fig. 6 for the Ketetahi gases indicates an apparent temperature of CO_2-CH_4 equilibration of 410± 10°C. To attain this values, the vapors would have had to reside at this temperature for about 100a. For the Hipaua-Tokaanu gases a lower temperature of 350±10°C is suggested, requiring a residence time of about 300a. The three areas occupy distinct positions, largely reflecting differences in the isotopic composition of the CO_2, about -8,0‰ at Ketetahi, -6.5‰ at Red and Central Craters, and -4.5‰ at Hipaua-Tokaanu. The difference between Ketetahi and the other Tongariro discharges mirrors the difference in relative N_2, He and C02 contents of Fig. 5 and suggests somewhat different origins or histories for the two sets of discharges. The agreement in the isotopic compositions of CO_2 and CH_4, and also of H_2S (Table 3), in gases at Hipaua and Tokaanu again supports a close link between the two areas.

Table 3 - Isotopic compositions of CO_2, CH_4, H_2, H_2O and H_2S, in ‰, and $^3He/^4He$ ratios, R, normalised to the air ratio, R_A. Numbers in brackets are isotopic compositions of serial condensate samples.

No	date	t(°C)	$\delta^{13}C-CO_2$	$\delta^{13}C-CH_4$	δ^2H-CH_4	δ^2H-H_2	δ^2H-H_2O	$\delta^{18}O-H_2O$	$\delta^{34}S-H_2S$	R/R_A
Ngauruhoe										
N1	780701	520	-11.2				-41.5	+2.64	+4.4	6.7
N2	790224	516	-9.6				-40.9	+1.10	+4.8	7.1
Red Crater										
R1	730909	96	-6.6	-23.5	-153		-44.7	-3.61,	+5.0	-
R2	740921	95	-6.0	-23.6	-142	-523			+3.1	
R3	750901	95	-6.8	-23.6	-139	-540	-42.2	-2.95	+2.9	-
R4	760417	95		-	(-33.2	-1.85)	-37.5	-2.15	+3.4	-
R6	790224						-43.7	-3.97		
Central Crater										
C2	740922	96	-6.7	-23.9	-142	-542			+2.9	-
C3	750901	95	-6.8	-23.8	-141	-527	-56.2	-4.55	+2.3	-
C4	760417	96	(-82.0	-12.98)	(-74.5	-11.28)	-68.2	-10.24	+3.6	-
C6	790224						-93.9	-14.60		
Main vent										
M1	730909	132	-8.5	-25.0	-157	-492	-48.5	-2.91	+2.9	-
M2	740921	132	-7.2	-25.1	-147	-539	-42.7	-2.20	+2.8	-
M3	750901	128	-8.7	-25.1	-149	-511	-52.5	-2.88	+2.3	-
M4	760417	136					-44.8	-2.16	+3.1	
M5	771207	-	-7.9	-26.5	-178	-501			+2.9	-
M6	790914	136	-7.7	-25.0	-155	-495	-44.7	-2.89	-	5.9
M8	830504	119	-7.8	-25.5	-158	-500			-	5.8
Eastern Vent										
E2	740921	118	-8.4	-25.2	-171		-94.9	-14.51	+1.8	-
E3	750901	128	-8.7	-25.1	-149	-511	-52.7	-4.61	+2.1	
E4	760417	128					-58.4	-4.90	+2.9	-
E5	771207	120	-8.2	-25.0	-164	-481				
E6	790224	98					-50.1	-4.32	-	5.1
Hipaua										
H1	940914	91	-4.6	-26.1	-148		-59.3	-8.40	+5.0	3.5
Tokaanu										
T1	790225	80	-4.8	-24.8	-144				+5.0	3.4
T2	790225	73	-4.3	-25.5	-139		-60.0	-8.00		

In Fig. **6B,** $^3He/^4He$ ratios, normalised to air, R_A, are plotted versus $\delta^{13}C$ of CO_2. It **also** contains points representing discharges **from** Ngauruhoe, **no** He isotopic data are available for Red and Central Crater. The data points describe a linear trend with $^3He/^4He$ ratios decreasing with increasing $\delta^{13}C$ values from Ngauruhoe over Ketetahi to Hipaua and Tokaanu. The decrease in R/R_A would suggest increasing interaction with crustal rocks or increasing residence times of the gases underground. At present there is **no** ready explanation for the differences in ^{13}**C-values.** The general distribution of data points, however, confirms the overall grouping of the discharges. Figures 6A and **B** also contain points (MT) representing gas bubbling along the shores of Lake Taupo at Motuoapa (Giggenbach et **al., 1993).** Its position within the Hipaua-Tokaanu group confirms a possible link between theses systems along the shores of Lake Taupo, **as** suggested by Mahon and Klyen (1968) **on** the basis of water **analyses.**

4. Conclusions

The thermal waters at Tokaanu have the highest Cl and **B** contents of all geothermal discharges over the Taupo Volcanic Zone. B is volatile at high temperatures and therefore is enriched in waters affected by interaction with high-temperature vapors. Nearby hydrothermal systems representing potential conduits for such high-temperature vapors, are Hipaua, **3 km** to the W, and Ketetahi, some 20 km to the **S.** The isotopic composition of steam condensates and of inferred deep waters are compatible with derivation of the Tokaanu waters from either area. Measured B contents in vapor discharges, and correlations among the enrichment of steam-heated pools at Ketetahi and Hipaua in ^{18}O and B, allow the B content of any deeper parent water to be estimated. They are **with 3660** to 7900 mg/kg at Ketetahi by far too high to be the **source** of a Tokaanu water with only about 100 mg/kg. B contents inferred for a deep Cl water at Hipaua are, after some dilution, comparable with Tokaanu waters.

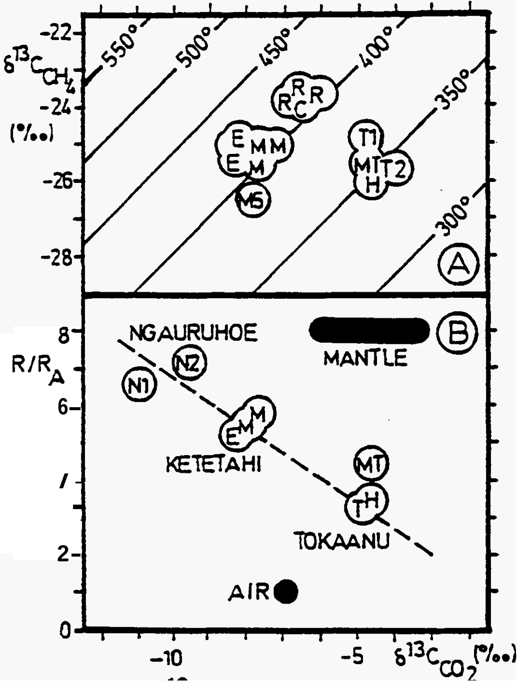

Figure 6- Plots of $\delta^{13}C-CH_4$ **(A)** and R/R_A (B) **versus** $\delta^{13}C-CO_2$ at Tongariro and Hipaua-Tokaanu.

Strong support for a link between the Tokaanu and Hipaua hydrothermal systems, as suggested by Seveme (1995), is provided by consistent differences in the chemical and isotopic compositions of CO_2, H_2S and CH_4, and the $^3He/^4He$ ratios between Tokaanu-Hipaua on the one side, and vapors discharged from Ketetahi, Red Crater and Central Crater, on the other.

Both systems, that comprising Tokaanu-Hipaua, possibly extending to Motuoapa, and that centered on Tongariro, appear to be of the arc-type, associated with andesitic magmatism, but are otherwise independent. Thermal activity has not changed significantly at all these areas over the last 60 years, and possibly the last 100 years. The Ketetahi thermal system, or even the Tongariro Thermal System generally (Hochstein and Bromley, 1979), appear to have remained essentially unaffected by the 1869 to 1896 eruptions from the Te Man craters (Friedländer, 1899) and the 1855 to 1859 eruptions in the Red Crater area (Gregg, 1960). In view of the potentially disastrous effects volcanic or hydrothermal eruptions from any of these systems may have on power installations in the area, it appears essential to obtain a good understanding of the nature of these systems and possible correlations among them.

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