Geochemical and Hydrological Assessment of Thermal Features in the Vicinity of the Champagne Pool in the Waiotapu Geothermal System

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ABSTRACT

Waiotapu thermal area is located within the Taupo Volcanic Zone of Central North Island of New Zealand. It has the largest area of surface thermal activity and has been the subject of various investigations.

In this paper water chemistry was used to evaluate the compositions of water from nine springs in the vicinity of the Champagne Pool. The spring waters can be classified into three groups: neutral chloride waters, mixed sulfate-chloride waters and sulfate waters. Constant mass ratios of CI:B in spring waters show a narrow range suggesting a common deep source.

Surface temperatures are near boiling with a maximum of 97°C. K-Na geothermometry indicates subsurface equilibrium temperatures of up to 297°C. Silica geothermometry is less reliable due to the diluted nature of water springs, but gives a maximum value of about 210°C.

The Champagne Pool and the Weather Pool have increased in CI and SO4 concentrations by about 100 ppm since their analysis in 1983.

This paper about water chemistry delineates the most probable location of the upflow zones, where the deep chloride water ascends to the surface in the vicinity of Champagne Pool.

1. INTRODUCTION

The Waiotapu geothermal area is located 40 km northeast of Wairakei and 25 km southeast of Rotorua. It is one of the 20 major hydrothermal regions in the Taupo Volcanic Zone (TVZ) of New Zealand. Its characteristics are similar overall to the other geothermal systems in this area not directly related to volcanic discharges (e.g Broadlands and Wairekei, Hedenquist, 1986). This is due to the relative similarity of the hosts rocks (largely flat lying silicic volcanic underlain by Mesozoic greywacke basement) and the domination of the meteoric water recharge in these systems, variations in gas concentration may be attributed to a variable magmatic input at depth (Giggenbach;1986, 1998).

Waiotapu eventually became known for its wide variety of hot springs, Champagne Pool, its collapse holes and crater lakelets, and its mud volcanoes, one of which was the largest in the entire district (Herbert, 1921).

The aim of this study is to develop a geochemical and hydrological assessment in the immediate vicinity of the Champagne Pool and describe a possible change in fluid chemistry based on the analysis of spring compositions at the Waiotapu geothermal system.
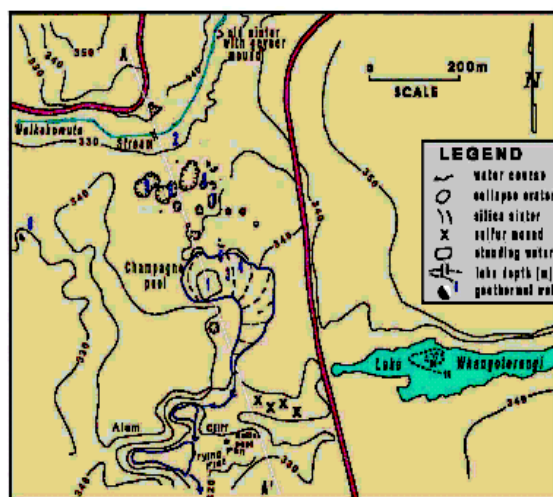

Figure 1: Sketch map of the Champagne Pool area in the southern portion of Waiotapu, surface features and sample localities (From Simmons and Browne, 1991)

2. STUDY AREA

The Waiotapu Geothermal field, an active epithermal mineral depositing system, is one of the largest (18 km^2) and most complex within the TVZ (Hedenquist, 1986). Complex surface activity includes large areas of surface alteration due to acid-sulfate fluids, steaming grounds, fumaroles and associated collapse craters, mud pools, silica deposits, notably the large silica (sinter) terrace, hot pools, and hydrothermal eruption craters especially Champagne Pool, the largest chloride discharge feature at Waiotapu.

This report describes the result of the geochemical study of thermal features in the vicinity of Champagne Pool and to construct a geochemical model using geochemical tools to interpret spring chemistry.

3. METHODOLOGY

In the preliminary investigation of a hot water in geothermal areas the most useful chemical data for interpreting the underground conditions are obtained from boiling springs which flows over 0.5 l/sec. These are likely to have undergone various amount of dilution, surface evaporation, and extensive interaction with surface rocks. In the absence of boiling springs, springs of lower temperature with small flows or even stagnant springs may give some useful information.

Water samples were collected and filtered (<0.45um) before storage in polyethylene bottles. Temperatures were measured and flowrates were estimated for springs. For the determination of pH and bicarbonate, 250 ml of unfiltered

water were collected and stored in bottle fitted with a rubber tubing and tightly clamp at the end.

Table 1: Springs and their description

Name / Date Collection	Temp. ºC / Flowrate l/s	Description
Champagne Pool 22/08/96	72 8 – 10	70 m diameter with liquid discharging at 75ºC, yellow to orange precipitate deposits on the margin of the pool, hydrothermal eruption breccia rim the pool and several patches of yellow fumarolic sulfur mixed with black sulfur occur on the sinter
Weather Spring 22/08/96	96 5	no silica sinter, clear pool
Black sulfur 22/08/96	97 -	vigorously bubbling spring, siliceous deposites, contain native sulfur
Opal Pool 22/08/96	15 <1	water yellow green in color, presence of yellow deposits, downstream of outflow
Artist's Palette 22/08/96	73 <.1	clear blue coloured pool with a yellow terrace of silica sinter stained by algae and yellow mineral deposits associated with arsenic, antimony and sulfur
Sulfur Cave 22/08/96	97 -	vigorously bubbling, clear water, presence of sulfur

Sampling techniques for boiling and warm springs vary accordingly to the constituents that are being investigated. Certain constituents such as silica may precipitate as the water cool, acidification to a pH less than 3 is done by adding 3 ml of 4N nitric acid per 500 ml of sample after collection to prevent precipitation of silica.

Major cations and uncharged species including silica, sodium, lithium, iron, boron, magnesium, calcium were determined using ICP-AES. Potassium were determined using Atomic Absorption Spectrophotometry. Undiluted sample was added with 2 ml of 1000 ppm CsCl to suppress any interfering elements. Sulfate was determined by colorimetric method using CE 373 Readout Grating Spectrophotometer at wavelength 450 nm. For chloride (Mohr Method) were an aliquot of sample is titrated against standard 0.1 N silver nitrate solution using potassium chromate as an indicator.

When the pH of the sample is adjusted to 8.25 at 25 ^{0}C, the total carbonate in the water is essentially in the form of bicarbonate (HCO_3). By adding a known volume of acid, the pH is brought to 3.8 and all the carbonate is in the form of CO_2. The CO_2 is removed by bubbling with CO_2-free air or nitrogen through the sample. The pH of the solution is then readjusted to 8.25 by adding carbonate free NaOH and further acid titration from 8.25 to 3.8 is made. The total carbonate in the sample is equivalent to the difference in the two titrations.

Where a complete analysis of a water sample is made, a check of the accuracy of the results is obtained by comparing the sum of the anion equivalents with that of the cations. Molecular ratios or atomic ratios are preferred to the weight ratio, since they reflect the proportions in which the constituents react with rock minerals.

Analytical results are expressed as milligrams per liter since most of the analyses are done in volumetric basis.

Four samples were taken and subject for X-ray diffraction analysis using Phillips X-ray diffractometer with nickel filter and CuKα radiation at 40 kv and 20 mA. This analytical technique was used to understand the relationship between the chemistry of fluid and the occurrence of alteration minerals.

Table 2: Common minerals identified by X-ray diffractions

Location	Sample No.	Minerals
Artist's Pallete	5	Sulfur, Jarosite, Barite, Pyrite, Cristobalite
Collapsed crater	7	Sulfur, Barite, Kaolinite, Grypsum
Rainbow crater	8	Sulfur, Alunite, Natroalunite, Quartz, Kaolinite
Spring (catchments)	9	Sulfur

4. GEOCHEMISTRY

The chemical analyses of springs are given in Table 3. There is a good ionic balance..

Table 3 Chemical composition of selected areas in the vicinity of champagne pool

Source	pH	HCO3	Cl	SO4	Ca	SiO2	Mg	Na	B	Li	Fe	K	% charge
1	5.5	63	1994	113	33	397	0.09	1066	24	9	0.49	182	-7.2
2	2		946	1112	19	297	2.14	573	11	5	4.84	117	-30.8
3	5.8		1385	178	21	299	0.22	743	16	6		150	-8.4
4	3.3		1656	144	27	300	0.21	893	20	7	0.09	165	-6.6
5	5.8	53	1385	180	24	271	0.34	746	17	6	0.17	150	-10
6	2		912	1075	18	289	0.63	553	9.7	5	5.42	113	-29.6
7	1.9		169	1500	11	273	1.68	83	1.3	0.6	16.9	48	-7.6
8	2		372										
9	2.4		946										

The waters were then evaluated using some well-known geothermal tools which classified the aqueous components into reactive and non- reactive species.

On the Cl-SO_4-HCO_3 figure 2 springs 1,3,4,and 5 cluster on the chloride apex while spring 7 plots on the surface corner. Thus waters from spring 1,3,4,and 5 are neutral chloride waters and spring 7 is sulfate water. Springs 2 and 6 are mixed sulphate-chloride waters. The low pH and comparably high sulfate of water 2 and 6 are more likely to have formed through mixing between chloride with sulfate waters. The discharge of the water with the highest chloride concentration is centered on the vicinity of champagne pool.
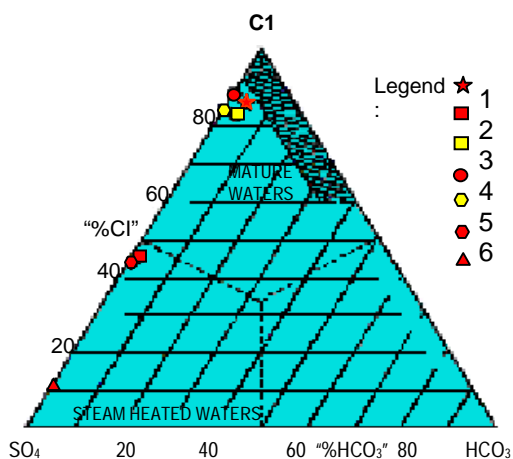
Figure 2: Cl-SO$_4$-HCO$_3$ diagram, alkali chloride spring waters plot on the chloride apex and steam-heated water in sulfate corner

The ratios of Cl:B, Na:K, Cl:Li and Na:Li show a narrow range for each group of spring waters, suggesting a homogenous deep figure 3. This is substantiated by the cluster of points in the plot of chloride against two other conservative elements boron and lithium. Spring 7 plot on the B apex indicates rock dissolution. The boron content of thermal fluids reflect to some degree of maturity of a geothermal system. Like As, Sb, and B expelled during the early heating up stages because of its volatility (Giggenbach 1991)Therefore, fluids from "older" hydrothermal system can be expected to be depleted in B apex.
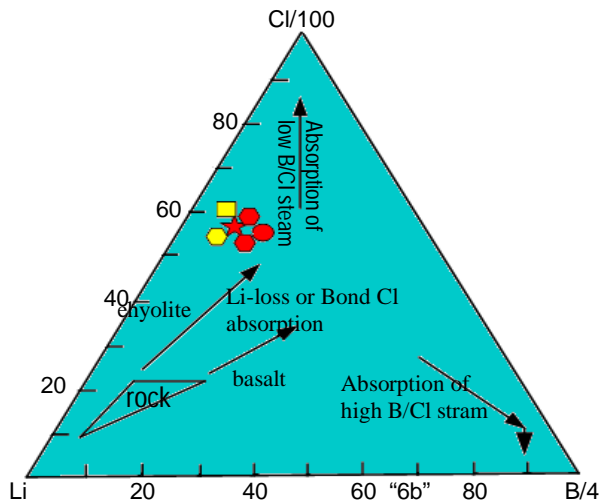

Figure 3: Cl-Li-B plot, showing spring 7 on the B apex indicates absorption of high B/Cl steam

From the Na-K-Mg plot figure 4 (Giggenbach 1988) spring 1 has attained full equilibrium while springs 3,4,5, & 6 point to the attainment of partial equilibrium. Spring 1 plot close to the full equilibrium line at the equilibration temperature of 280 ^{0}C. Samples plot off the equilibrium line indicating attainment of only partial water-rock equilibrium. All the acid waters are shifted towards the points marked "rock dissolution" reflecting the immature nature of these waters.
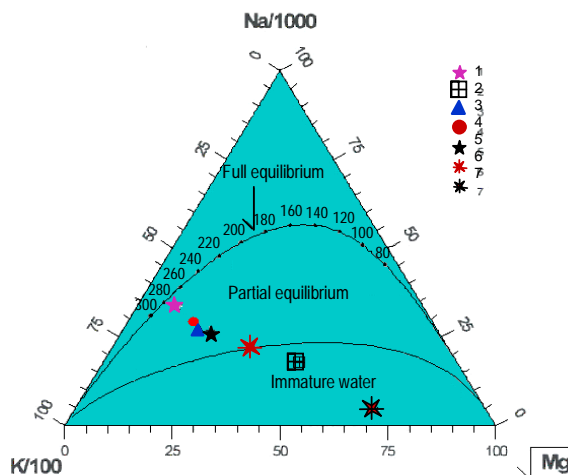

Figure 4: Plot of relative Na-K-Mg concentrations showing the fluids of champagne pool in full equilibrium

5. GEOTHERMOMETRY

In Table 4 shows results for the reasonable geothermometers used for the spring waters. These are quartz, Na-K, and Na-K-Ca , the choice of quartz geothermometer is based on the fact that in all rocks at temperature >180 ^{0}C quartz tend to be the controlling mineral concentration.

Table 4 : Indicated temperatures from chemical geothermometers.

Source	SiO2	Chal	Cond	Adia	Na-K F	Na-K G	K-Mg	Molecular Ratio				
								Cl/B	Cl/Li	Na/Li	Na/K	B/Cl
1	108	220	232	210	268	279	42	85	228	122	5.86	0.01
2	84	192	209	191	287	297	84	89	204	124	4.89	0.01
3	84	195	209	192	286	295	35	86	235	126	4.95	0.01
4	84	193	209	192	276	287	35	83	234	126	5.41	0.01
5	77	184	202	186	285	295	43	84	233	123	4.97	0.01
6	82	189	207	189	287	296	56	94	199	121	4.89	0.01
7	78	183	202	186	420	426	78	129	277	135	1.73	0.01

The Na-K-Mg triangular plot indicates that the waters have equilibrated with the odium and potassium minerals. As such the use of the Na-K geothermometer is justified. Subsurface temperature estimates from 268 ^{0}C to 299 ^{0}C.

6. HYDROLOGY

Figure 5 shows the hydrological model, mixing the deep chloride waters with shallow groundwater. Boiling results in the formation of steam-heated waters which dilute, through mixing the ascending water. The primary component of the ascending fluid discharges as the champagne pool being the principal focus of chloride discharge. When the ascending fluid reach the surface of the system, mixing with surface groundwater accounts for the dilution trend apparent from spring sampled.

7. PRESENT & PREVIOUS STUDY-A COMPARISON

Analyses of waters from the same springs, champagne pool and weather pool compared to previous survey shows that there has been an increase in relative concentration in SO$_4$ and Cl concentration by about 100 ppm since their analysis in 1983. Present and previous studies of these springs shows no marked difference in the magnesium content.
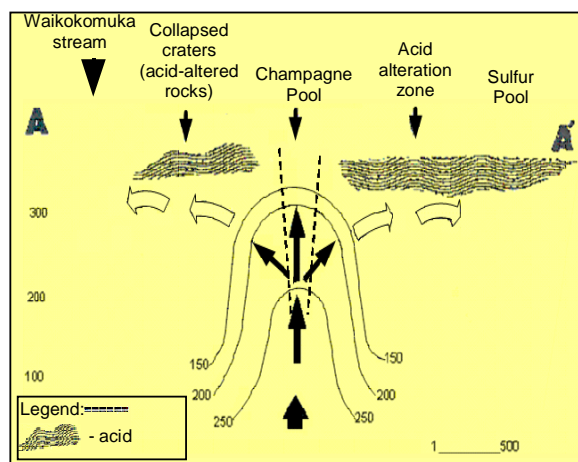
Figure 5: Cross section along line A-A' looking north east

Table 5 : Comparison of spring chemistry in mg/kg

Champagne Pool	Temp ^{0}C	pH	Cl	SO4	SiO2	Mg
Previous	75	5.5	1896	53	445	0.05
Present	72	5.5	1994	113	397	0.09
Weather Pool						
Previous	99	2.1	914	756	341	1.20
Present	96	2.0	946	1112	297	2.14

Previous chemical compositions of the selected hot springs present in the individual thermal features identified at Waiotapu by Lloyd (1959), Wilson (1963), and Sheppard and Robinson (1980) and these were sampled in 1983.

8. SUMMARY AND CONCLUSION

This report of water geochemistry delineates the most probable location of the upflow zone, wher the deep chloride water ascends to the surface in the vicinity of champagne pool.

Spring waters in survey area in Waiotapu are neutral chloride waters, acid-sulfate water and mixed sulfate water. Acid sulfate water occur in spring 7, its acidity is due to prolonged contact of H_2S with oxygen producing sulfate and other gases derived from the boiling fluid at depth being transported to the near surface by the steam. This acid water also mix with chloride waters at very shallow depth before they discharge to the surface. Oxidation of hydrogen sulfide in surface water has produced a wide range of acid-sulphate chloride water together with deposits of elemental sulfur, which can be found in springs 2,6, & 7 . High chloride springs with low pH can be due to the steam rising through the water or the effect of subsurface sulfur deposits. These are located in spring 2 & 6 , these springs have discharge temperature at or near boiling and have aprons of amorphous silica sinter.

Defined by the fluid chemistry, the least diluted surface discharge of the deep ascending fluid is from champagne pool. Chemical evidence indicates that this water has boiled upon ascent. Other chloride springs have been diluted by a steam-heated waters.

The K-Na geothermometer indicates temperature up to 299^0C, however the more rapidly equilibrating K-Mg geothermometer indicates cooler temperature, due to re-equilibration following dilution of chloride waters by the shallow and marginal steam heated water. Silica geothermometry is less reliable due to the diluted nature of many springs.

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