

CYCLIC AND TEMPORAL CHANGES IN WATER CHEMISTRY OF INFERNO CRATER, WAIMANGU GEOTHERMAL VALLEY, NEW ZEALAND

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ABSTRACT

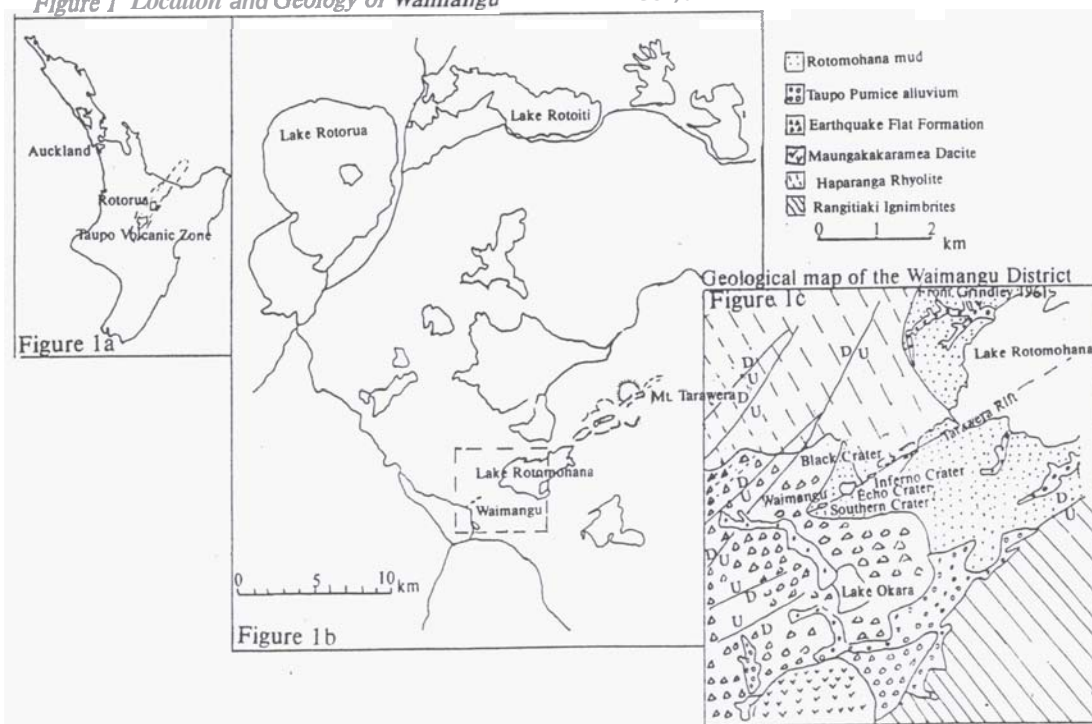
The Waimangu Thermal Valley was exposed as a consequence of the eruption of Mt Tarawera on June 10, 1886. The cyclic nature of geothermal activity in the valley was demonstrated by the Waimangu Geyser which played with a 36 hour period from 1900 to 1904, and is exhibited today by the Inferno Crater Lake. Inferno Crater lake is located in the side of Mt Hazard (a small rhyolite dome) 15m above other features in the valley. The lake water is a chloride fluid that has undergone 29% mixing with an acid-sulphate fluid. HCO_3^- is a minor component. Inferno Crater lake undergoes a quasi-cyclic movement in water level and temperature over a six week period. However from January to May 1990, a temporary cycle of frequent minor overflows was established. A geochemical survey over this period revealed Na, K, B and Li show a sympathetic variation in concentration with Cl, while Si, Ca, Fe, Al, NH_3 and Mg vary sympathetically with SO_4 . Correlations between fluctuations in temperature, SO_4 concentrations and mass flow suggest that condensation of a steam into the lake is the dominant factor controlling the cyclic behaviour of the lake.

Introduction

Waimangu Thermal Valley is situated in the Taupo Volcanic Zone of the North Island of New Zealand, 26 km south of Rotorua (Fig 1). Prior to the eruption of Mt Tarawera on June 10, 1886, thermal activity in the Waimangu valley was absent. Instead geothermal activity was restricted to the then smaller and cooler Lake Rotomohana, the site of the famous Pink and White Terraces (Hochstetter 1864). With the eruption of Mt Tarawera and Lake Rotomohana these terraces were destroyed as a line of craters opened in a south-westerly direction from Tarawera, through Lake Rotomohana, and up the Waimangu Valley to form the Tarawera rift (Naim 1979). Thermal activity in the valley began 10 years later (R.F. Kearn, pers. comm. 1989).

Today Waimangu is an area of diverse and intense thermal activity and includes near-neutral-pH chloride springs (boiling, geysering and spouting), acid sulphate springs and springs discharging mixed waters. An unusual aspect of geothermal activity at Waimangu is its cyclic nature. This was displayed by the Waimangu geyser that played with a 36 hr period from 1900 until 1904 (Stanton, 1978), and is demonstrated today by the Inferno Crater Lake which shows a quasi-cyclic movement in the lake level and temperature (Scott et al 1982).

Figure 1 Location and Geology of Waimangu



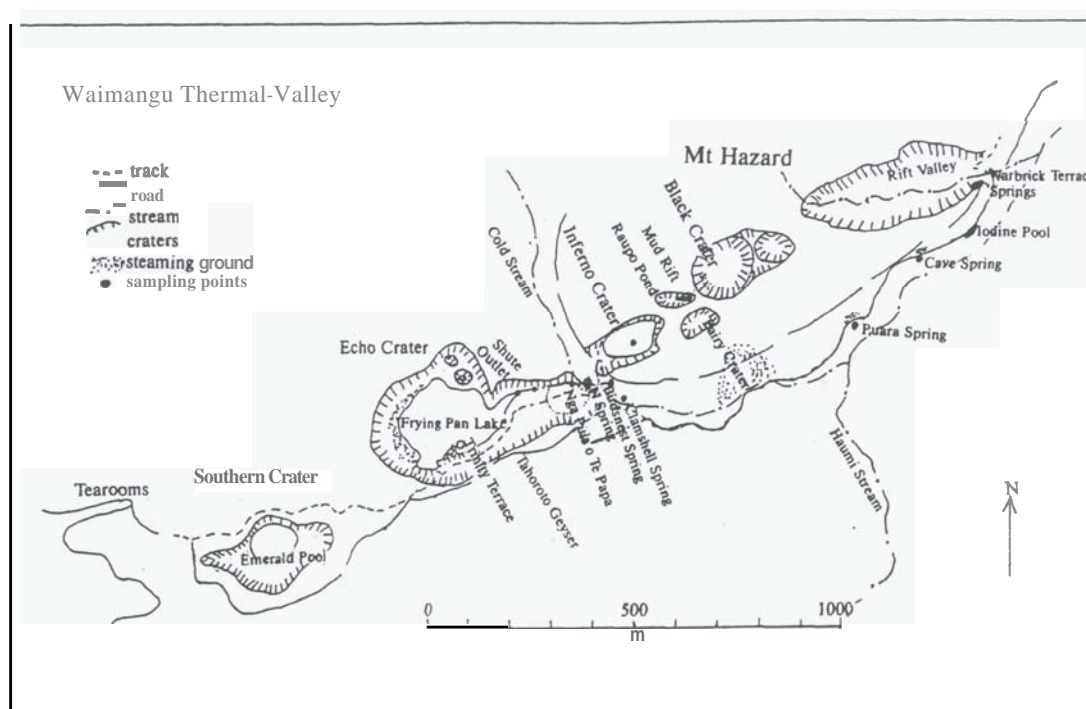


Figure 2. A map of features in the Waimangu Thermal Valley

The present study was initiated to investigate whether the water chemistry of Inferno Crater could offer any insight into explaining this unusual behaviour.

Geology

The surface stratigraphy (Fig. 1c) of the Waimangu Valley comprises predominantly Rotomohana Mud ejected from the Rotomohana Crater of the 1886 Tarawera/Rotomohana eruption (Thomas 1888). This material is up to 20m thick in road cuttings in the valley, and in places its lower boundary can be seen overlying the 1886 palaeosol and Taupo Pumice eruption material. Deposits of hydrothermally altered country rock ejected by the Waimangu Geyser and by hydrothermal eruptions from Echo Crater are visible in roadcuttings in the north-west of the valley. Inferno crater (Fig. 2) is located in a sub-circular crater excavated from the side of Mt Hazard, a small rhyolite dome that is also host to the Black and Fairy Craters.

The subsurface geology of Waimangu is inferred from ejecta from hydrothermal eruptions and exposures outside of the geothermal field. Earthquake Flat Breccia occurs as altered blocks throughout the valley and is most common around Echo Crater. It comprises the Cathedral Rock, and is found to be an important constituent of material ejected by the 1917 eruption of Echo Crater and the 1973 Trinity Terrace eruption.

Rangitaiki Ignimbrite is inferred to lie beneath Earthquake Flat Breccia since a large proportion of clasts collected from Trinity Terrace eruption material are comprised of this lithology. The Rangitaiki Ignimbrite is approximately 60m thick with its upper surface as near as 30m beneath the floor of Frying Pan Lake (Lloyd and Keam, 1974).

METHODS

Sampling Procedures

This investigation involved a 14 week survey of the Waimangu valley thermal features including Inferno Crater. Samples were collected on a weekly basis using a 1 litre polythene beaker clamped to the end of a 6m pole. Samples were collected adjacent to where the

lake level and temperature monitoring equipment enter the lake. Samples were filtered through 0.45 mm millipore filter membrane. During periods of overflow, the water was very turbid disturbing the fine mud that lines the crater and this made filtering very difficult. Temperature and estimates of the lake level were noted. A 500mL unacidified and a 250mL acidified sample were collected for analysis of cations and anions respectively. During the latter third of the survey samples for HCO_3^- analysis were collected in a glass vessel with a butyl rubber tube neck (provided by D.S.I.R. Chemistry, Wairakei). Analyses were carried out in the chemistry laboratory of the D.S.I.R. Chemistry (Wairakei) the following day.

Analytical Techniques

A large proportion of the analysis was performed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES); using this technique B, Si, Na, K, Ca, Mg, Al, Fe, Li and S were determined. The instrument was calibrated daily using standards prepared from dissolved metals or purchased standards. Checks on instrumental drift were made using repeated analysis and analysis of a standard every twenty samples. Each element was determined three times and a precision of 5% was estimated for the technique.

Rubidium and Cs concentrations were determined by Atomic Emission Flame Spectroscopy. The Rb analysis used a Rb lamp at a spectral band pass of 0.1nm. Standards were prepared by dilution of a stock solution of Rb_2CO_3 in NaOH/EDTA (used to approximate the saline composition of the geothermal fluid and to mask the effect of interferences such as Mg). Samples were diluted by ten times in this same NaOH/EDTA solution. Cs was analysed with a Varian Tectron lamp at a spectral band pass of 0.1nm. The ratio of acetylene to air was adjusted to give maximum emission. A stock solution of 100mg/kg Cs was prepared from CsCl. Standards and samples were prepared and analysed as outlined for Rb analysis. Instrumental drift was checked for both elements by analysis of a standard after every 10 samples resulting in a precision of 8% for the technique. This is slightly higher than the precision of ICP-AES due to the low concentrations of Rb and Cs present.

Sulphate was determined colorimetrically on a Schmadzu Double Beam Spectrophotometer UV190 at a wavelength of 380nm. The technique is based on the reaction of sulphate with BaCrO_4 to form insoluble BaSO_4 , liberating chromate ions which are determined colorimetrically (Giggenbach et al. 1986). Samples with sulphate concentrations greater than 100mg/kg were diluted. Total S was analysed by ICP-AES and there is good agreement between these and sulphate concentrations, indicating the presence of only very low concentrations of other S species. The instrument was calibrated using standards prepared from K_2SO_4 crystals. The technique involves a great deal of sample manipulation and therefore room for large errors. To check this and any errors involved in calibration, four reference standards were analysed with each calibration. This provided a precision estimate of 11% for the technique.

Chloride was analysed by Mohr titrations. This procedure involves the titration of a known aliquot of sample with a solution of 150mg/kg (approx.) AgNO_3 ; $\text{KCrO}_4/\text{K}_2\text{Cr}_2\text{O}_7$ indicator was used and the endpoint was signified by the initial formation of red AgCrO_4 (Vogel 1986). A standard was analysed every 10 samples and a precision of 10% was attained.

Ammonia was measured using a gas sensing Ammonia Electrode (Orion Research Ammonia Model 95-10). The technique measures the activity of dissolved ammonia gas in aqueous solution. Ammonium ion is converted to ammonia by the addition of NaOH until the sample had a pH of greater than 10. The electrode was calibrated using the method prescribed for low level measurements in the electrode manual (Orion 1979). Fresh standards were prepared from a 1000 mg/kg stock solution of NH_4^+ (prepared from NH_4Cl powder) for each calibration. Each sample was measured three times and a standard was measured after every 10 samples. A precision of 5% is estimated for the technique. Instrumental drift was a problem due to the susceptibility of the electrode to changes in temperature caused by the magnetic stirrer. This was kept to a minimum however with the use of an insulating mat, and by recalibrating after every 15 samples had been analysed.

Bicarbonate was analysed at the Wairakei Geothermal laboratory of D.S.I.R., Chemistry using a pH titration method (Giggenbach et al. 1986). The procedure consists of an alkalinity titration corrected for the effects of other weak acids (boric and silicic acids) by a back titration. Precision was checked by the analysis of a standard after every 12 samples. This is estimated to be 10% for the technique.

pH was measured in the laboratory at 25°C using a portable pH meter, while temperature was measured in the field.

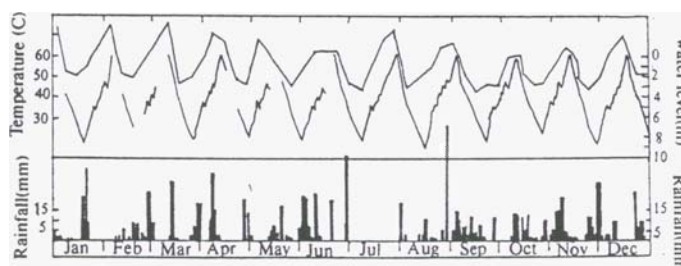


Figure 3. Hydrology Measurements of Inferno Crater for 1980

from Scott 1980

INFERNO CRATER LAKE

Cyclic History

The unusual cyclic behaviour exhibited by the Inferno Crater Lake has an approximate six-week period (Fig. 3), during which the water level oscillates between overflowing and down to 12m below the overflow level. During overflows lake water has a maximum temperature of 70°C, while at its minimum level it has a temperature of approximately 35°C. This behaviour is not a result of rainfall or climatic conditions (Scott et al. 1982). Four stages are observed in the cycle (Stanton 1978); the first occurs when the water level and temperature are at a minimum. The second is a period of in-phase water level and temperature oscillation superimposed on a gradual overall rise in both temperature and water level. The third stage involves the rise of lake level to produce a major overflow (3-5 days) and temperature increase to maximum temperature. Cessation of overflow and recession to minimum lake level (15-20 days) marks the fourth and final stage: There is a rapid decrease in temperature during this latter stage.

Inferno Crater exhibited this behaviour when the Waimangu Geyser played and was used to predict an impending eruption from the geyser (Stanton 1978). The cyclic behaviour has been continuously monitored since 1970 by the Tourist and Publicity Department, NZ Geological Survey D.S.I.R. and the Physics Department of Auckland University. This monitoring has included temperature and discharge measurements of the crater and has revealed that hydrothermal events cause disturbances to the cyclic behaviour of Inferno Crater. Overflows were missed on four occasions: 1973 Trinity Terrace eruption (Llyod and Keam 1974); 1975 N spring disturbance (Nathan and Keam 1975); 1978 Mud Rift Activity (Keam 1978) and 1981 Mud Rift eruption (Scott 1981). On other occasions disturbances could not directly be attributed to hydrothermal events; for example, from February to March of 1986 the cycle was disrupted when the lake level remained high, a series of 10 minor overflows occurred and a large volume of mud was deposited around the lake (Scott 1986). Although this style of activity had previously not been recorded it has recently been displayed. During the course of this investigation (from February to April, 1990) the lake level has oscillated between overflow and 1.5-2m below the overflow level. The temperature has remained between 70°C (when overflowing) and 60°C and there were six minor overflows from February to July of 1990.

Scott et al. (1982) have attributed this disrupted behaviour to changes in aquifer pressures, which, while affecting all springs in the valley, is more clearly seen in Inferno Crater because of its obvious cycling behaviour. A drop in pressure reduces overflow, while an increase in pressure induces greater overflow from the lake.

Previous Geochemical Investigations

There have been few studies of the water chemistry of Inferno Crater (Table 1). In an early study by Grange (1937) in which all geothermal features in the Rotorua-Taupo District were investigated, Waimangu Valley and Inferno Crater were given a detailed mention. Grange found Inferno Crater to have a silica concentration of 741 mg/kg and "appreciable" amounts of boron were reported. Mahon (1965) describes Inferno Crater to be acidic (pH 2-4), but otherwise chemically similar to the boiling springs in the valley. The acidity of the lake water is attributed to oxidation of H_2S which, with CO_2 , rises to the surface to give the impression of boiling.

Table 1. Previous chemical analysis of Inferno Crater

Date	T	pH	Li	Na	K	Rb	Cs	Mg	Ca	SiO2	B	NH3	F	Cl	SO4	HCO3	Al	Fe
a pre 1937	-	2.5	-	737	126	-	-	2	118	741	7	-	-	743.2	321.3	-	0.5	3
b 13/6/75	-	2.44	3.73	539	94	-	-	1.6	13.3	611	-	-	-	867	432	-	-	-
c 23/7/75	42	2.44	3.7	543	95	-	-	1.28	12.5	688	-	-	-	881	427	-	-	-
d 17/10/75	44	2.44	3.93	542	97	-	-	1.28	11.5	670	-	-	-	867	438	-	-	-
e 30/4/82	43	2.3	5.4	540	103	-	-	1.09	2.19	17	667	8.63	7.2	2.2	852	400	-	-
f 30/4/82	43	2.4	5.8	593	101	1.06	1.00	1.76	18	643	8	2	2.9	900	480	-	2.0	3.6

concentration in mg/kg a Grange 1937 b Glover 1975 c Sheppard 1986

Table 2. Chemical analysis of Inferno Crater for January to April 1990

date	T (C)	pH	Li	Na	K	Rb	Cs	Mg	Ca	SiO2	B	NH3	Cl	SO4	HCO3	Al	Fe
17/1/90	62.5	2.5	5.2	556.6	104.0	-	-	1.6	13.0	654.2	7.3	1.2	881.2	427.8	-	1.8	3.7
25/1/90	58.2	2.98	5.5	598.3	111.7	-	-	1.5	12.8	644.5	7.5	1.4	886.1	386.9	-	1.8	-
4/2/90	73.8	2.24	5.0	497.1	91.9	-	-	1.3	11.3	612.5	6.5	1.4	885.3	433.4	-	1.2	2.9
11/2/90	61.4	2.5	5.6	546.2	106.5	-	-	1.5	13.6	715.0	7.4	1.5	917.9	405.9	-	1.4	3.6
19/2/90	58	2.37	4.8	522.3	97.7	-	-	1.4	13.0	654.9	7.0	1.5	920.4	368.9	-	1.3	3.8
26/2/90	68.2	2.47	4.7	515.8	105.0	-	-	1.5	13.9	658.5	7.2	1.5	934.2	388.8	-	1.4	4.5
4/3/90	69.9	2.52	4.6	505.9	102.6	-	-	-	13.2	635.0	6.7	1.5	928.1	317.6	-	1.4	2.0
11/3/90	61.5	2.35	4.8	521.5	97.9	-	-	1.5	14.4	692.7	6.3	2.2	929.7	366.2	-	2.0	4.3
18/3/90	71.5	2.5	5.0	565.1	108.6	-	-	1.6	15.0	801.5	7.1	1.4	939.7	376.7	-	2.2	5.5
25/3/90	69.2	3	4.4	502.1	98.4	.1	.6	1.6	15.1	845.7	7.0	1.4	914.1	409.4	16.1	4.0	6.2
2/4/90	66.5	2.28	4.5	504.3	94.2	.1	.5	1.8	15.2	777.6	6.6	1.6	938.0	433.4	23.2	1.9	5.2
9/4/90	-	2.5	4.3	512.8	100.0	.1	.6	1.4	14.0	770.8	6.9	1.7	934.2	403.9	30.5	1.6	4.1
17/4/90	59	2.44	4.6	542.8	105.8	.1	.5	1.5	14.6	790.9	7.2	1.7	948.9	419.5	7.3	1.6	4.6
23/4/90	60	2.45	4.5	569.5	106.2	.1	.5	1.4	14.6	818.4	7.6	1.7	946.6	394.7	10.3	1.5	4.8

concentrations mg/kg

The outbreak of N Spring in **May** 1975 (Fig. 2) prompted the first chemical investigation of several springs over a period of time (Glover **1975**). One of the springs included in the survey was Inferno Crater. The lake showed little chemical change over a period of four months in **1975**, but Si, pH and Na/Li values were used to demonstrate that water from Inferno Crater is distinct from all other thermal features in the area.

The most comprehensive investigation into the chemistry of the valley was **performed** by Sheppard (**1986**). This investigation includes an analysis of Inferno Crater Lake when it was at a level of ten meters below overflow (a level not reached during the present investigation). Using various techniques including compositional trends, variations in isotopic compositions, temperatures, mineral and solution equilibria, a model of subsurface hydrological flow was **devised**. This placed Inferno Crater almost directly above the deep aquifer and shows the influence of mixing with mineralized water **from** the south, local meteoric water **and** steam flows.

AQUEOUS GEOCHEMISTRY JAN-MAY 1990
Mixing

Results of analyses **are** listed in Table 2. They show that Cl and SO4 **are** the major anions present, while Na and K **are** the major cations; Si has a high concentration (300mg/kg) and B, Ca, Li **are** less concentrated (**5** -10 mg/kg); **Mg**, Al, Fe, Rb, Cs and NH3 are only minor constituents; the HCO3 component is very low (<20mg/kg). **F**igure 4 shows that the fluid of Inferno Crater Lake is a mixed alkali-chloride/ acid sulphate fluid. This agrees with work by Sheppard (**1986**), whose analysis is **also** plotted on Figure 4.

The plot shown in Figure 5 was used to estimate the extent of mixing between sulphate and chloride fluids. A number of assumptions are made in the construction of the plot. For example, it **was** assumed that the Cathedral Rock spring with 1323mg/kg SO4 and very low Cl concentration (<10mg/kg) represents the unmixed sulphate end-member. There is no example of an unmixed chloride end-member in the valley, however, as Inferno Crater has the greatest Cl concenuation (**920** mg/kg) and very low HCO3 content (<15mg/kg), it is assumed that it lies on the Cl-SO4 mixing line and a

hypothetical chloride end-member is attained (1310mg/kg). Dilution by HCO3 can **also be** shown on this diagram. Bicarbonate can be introduced by a HCO3 fluid or by groundwater. The meteoric water at Waimangu (determined **from** analysis of stream water in the valley) is plotted for reference. The trend shown by several springs on the BB' line of Figure 5 indicates that dilution occurs with a HCO3 fluid, while those on the AC' and CC' lines indicate dilution with groundwater.

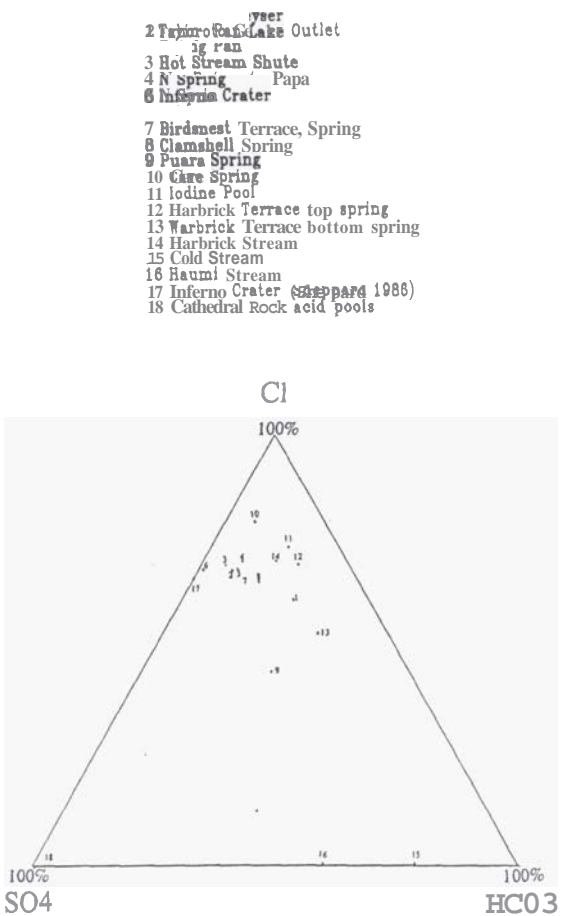
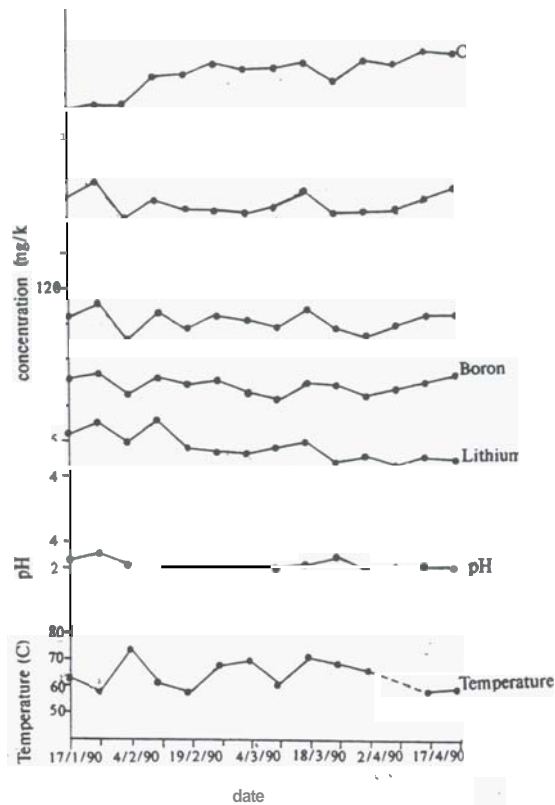


Figure 4. Composition of fluids from the Waimangu Thermal Valley



FIGURES. Elements that show a sympathetic change in concentration with Cl

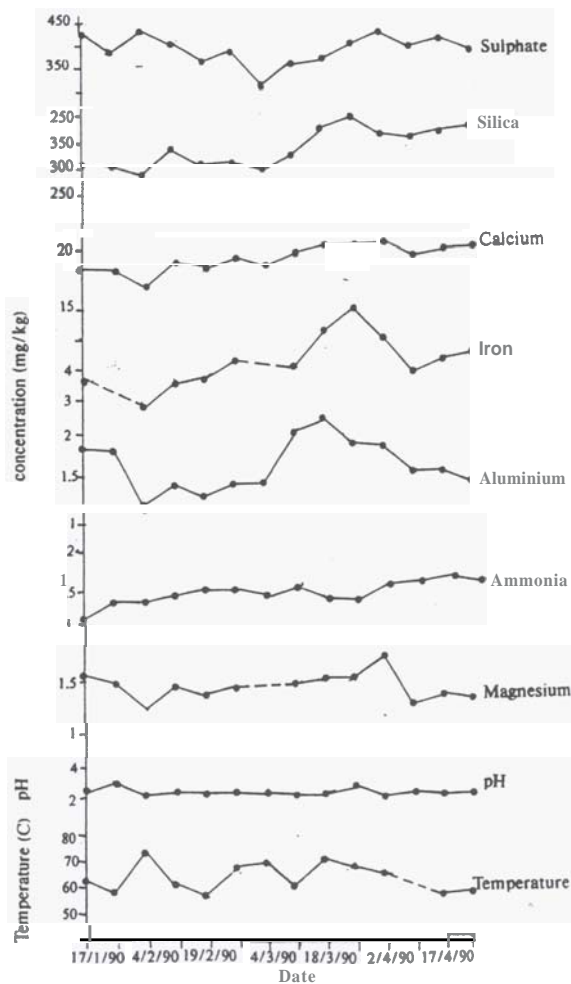


FIGURE 9. Elements that show a sympathetic change in concentration with SO4

Chloride-compatible elements (Fig. 8) show a gradual increase in concentrations from January-April, 1990, overprinting a series of minor small-scale fluctuations. Comparing this with lake level measurements in Figure 10a reveals this rise corresponds to the period of cycle disruption. The SO₄-compatible elements (Fig. 9) show a more obvious correlation With lake level measurements (Fig. 10b), with high water levels corresponding to increased SO₄ concentrations. In neither case, however, does this correlation concur with the results of Sheppard (1986) who reported Cl and SO₄ levels (900mg/kg and 480mg/kg respectively) similar to those found in this investigation, but when the lake was at a level of 10m below overflow. However the exact position of the lake level in the cycle at the time of Sheppard's sampling is not known as the hydrological records for this time are incomplete (Scott 1982), making direct comparison of Sheppard's data and analysis presented here difficult

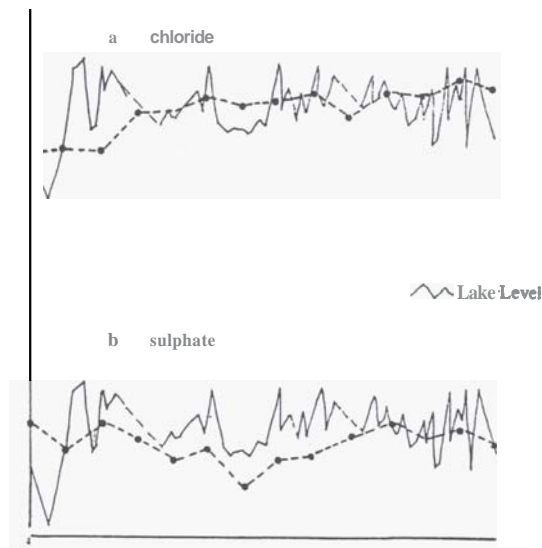


Figure 10. Schematic diagram showing variations in Chloride and Sulphate concentrations with cyclic behaviour of Inferno Crater

DISCUSSION

Spatial relationship of Inferno Crater to other geothermal features in the Waimangu Thermal Valley.

Cl/B ratios are constant throughout the entire valley (~ 10) indicating that all thermal features are fed by the same reservoir. Inferno Crater has the highest Cl content in the valley and its low Na/Li ratios (~100) compared with up to 200 (eg. N Spring) for other springs in the valley, suggests that Inferno Crater Lake water has a more direct path of migration to the surface and may be directly fed by a deep fluid. The high SO₄ concentration is explained by the elevation of the crater 15m above the other springs in the valley so that a deep area for steam condensate development is present. The Birdsnest Terrace spring (Fig. 2) is situated below Inferno Crater on the shore of the hot water stream and shows the next highest Cl and SO₄ concentrations in the valley. While the springs in the south-west of the valley also show appreciable SO₄ and low HCO₃ concentrations, those in the north-east of the valley show low SO₄ and high HCO₃ concentrations, suggesting the dominance of a perched SO₄ fluid in the south-west and a dominant HCO₃ fluid in the north-east. Using this information a cartoon depicting how Inferno Crater fits into the valley can be constructed (Fig. 11). This is similar to that proposed by Sheppard (1986).

Cyclic Behaviour of Inferno Crater

The correlation of increasing sulphate concentrations with increased lake levels (Figure 10b) suggests the importance of a steam component in the cyclic behaviour of Inferno Crater. An increase in steam within the lake introduces a larger H_2S component which oxidises causing an increase in SO_4 concentration. The steam would also add to the mass and enthalpy of the fluid in Inferno Crater Lake causing the water level and temperature to increase. This model is supported by the geochemistry of the lake water: Cl concentrations remain approximately constant while changes in SO_4 concentrations can be tied into measurements of water level and temperature of Inferno Crater Lake. This suggests that the mass of condensate is the major control on element concentration and lake overflow. Inferno Crater must have a sub-surface chamber that is filled with Cl fluid; with increased steam condensation the lake level rises leading to an eventual overflow. This is followed by a fall in lake level as the chamber becomes depleted. The process is repeated as condensate level then builds up.

This hypothesis agrees with a model proposed by Stanton (1978) developed from a study of seismic noise in Inferno Crater. This model involves a heat supply by a constant flow of hot water from an aquifer underlying the Rangitaiki Ignimbrite. Stanton (1978) suggests a conduit connects the main vent of Inferno Crater to the aquifer and intrudes into part of the aquifer so that during the low level stage of the normal cycle the reservoir is occupied by a major part of the volume of water from Inferno Crater. Hence the fluctuations in lake level and temperature reflect changes in the thermal system beneath the lake. In Stanton's model these fluctuations are due to changes in the steam volume of the system rather than changes in reservoir or deep heat flow.

In a purely speculative manner, it is interesting to compare the cyclic behaviour exhibited by Inferno Crater to that of a geyser which traditionally has a narrow opening through which water is forced to produce an often spectacular eruption. If the vent of Inferno Crater was not a lake but instead a small pool then perhaps it would also exhibit geyser like activity.

CONCLUSION

Inferno Crater occupies an important position in the Waimangu Thermal Valley. The high Cl concentration of the lake water suggests that it is fed directly from the reservoir, and its high SO_4 concentration is a function of its elevation 15m above other springs in the Waimangu Thermal Valley. The cyclic behaviour exhibited by the lake is controlled by the production of a condensate as steam is introduced into a chamber below the lake. This increases the enthalpy (reflected in increased temperatures) and the mass of the fluid so the lake overflows. As the condensate is depleted, the lake level and temperature decrease and the cycle repeats. Steam may be introduced into the chamber by continuous boiling of a deeper aquifer. However the role of boiling and whether it is continuous, erratic or cyclic within a reservoir, is unclear. The suggestions made here are based on observations made over a relatively short time-span, and so only provide a brief glimpse into the processes that may be present. A long term geochemical investigation carried out over several of Inferno Crater's "normal" cycles may provide data to strengthen and expand these suggestions.

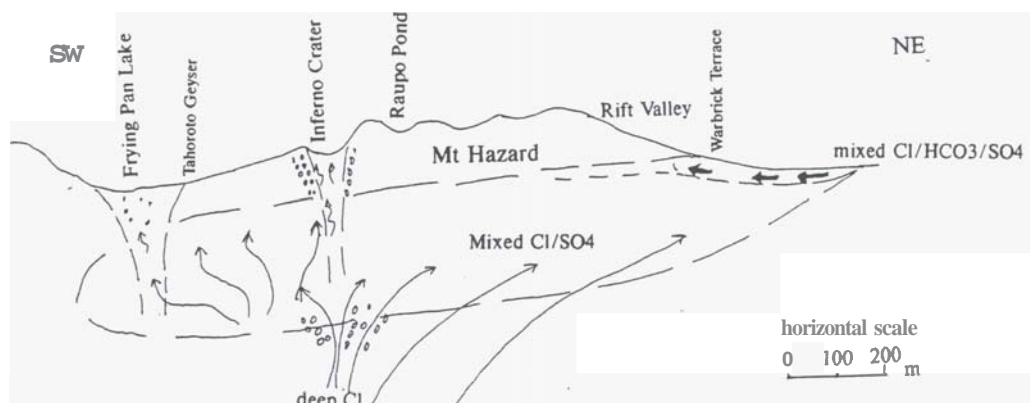
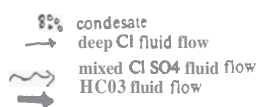


Figure. 11 Schematic diagram showing the hydrology of the Waimangu geothermal system



A deep Cl fluid rises and SO_4 condenses to produce a mixed Cl/ SO_4 fluid. This fluid feeds all springs in the valley. Inferno Crater taps into the mixed fluid where maximum condensation and upflow occur. The springs in the NE are also fed by a shallow HCO_3 fluid that mixes with the mixed Cl/ SO_4 fluid.

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