Chemistry of the Rotorua Geothermal Field Part 2: Discharging Wells – update of chemical and isotopic compositions and comparison with historical data

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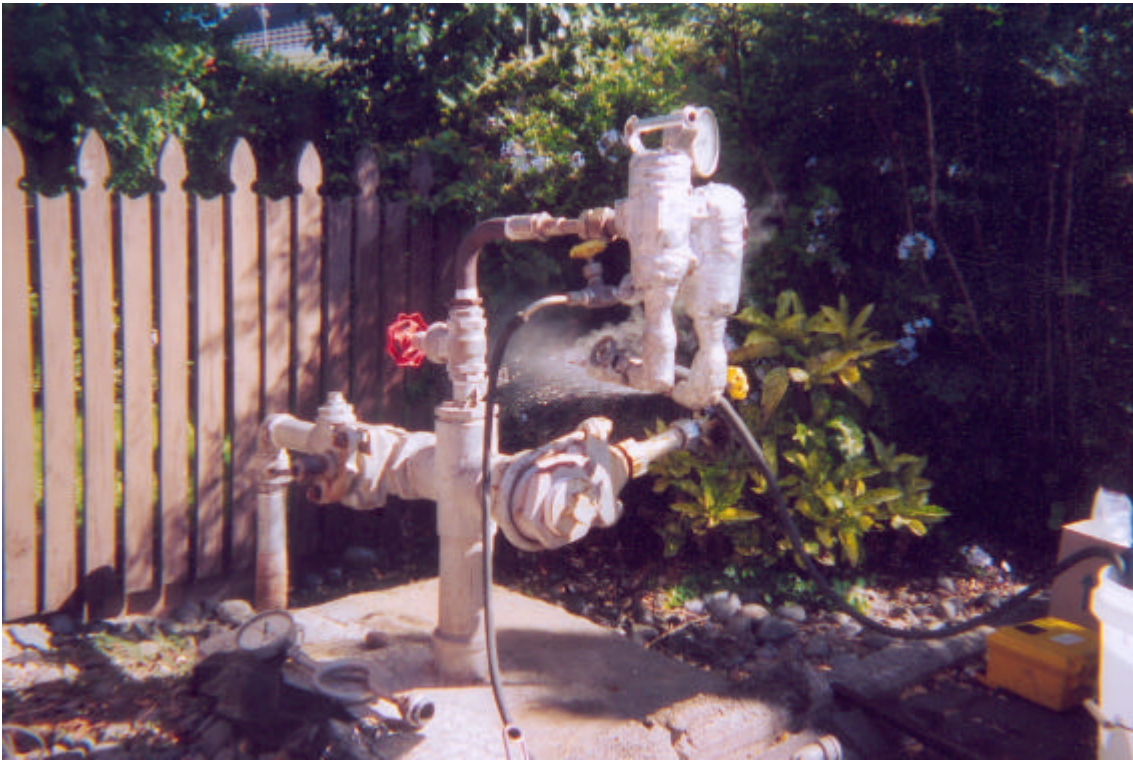B J Scott
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A webre separater in action on a Rotorua two phase well, showing the separation of the gas and water.

Sampling the gas phase of Well 601A in Rotorua by Karen Britten.

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EXECUTIVE SUMMARY

A geochemical survey of selected wells was undertaken for comparison with historical data and to determine aquifer relationships and reservoir characteristics of Rotorua Geothermal Field. This study follows and complements the previous geochemical survey of 31 selected Rotorua natural features, which provided an overall assessment of the recovery of the springs following the enforced bore closure programme undertaken since 1986.

We report the chemical and isotopic analyses of steam and water samples collected from 10 wells which were chosen to provide a wide geographical coverage across the field. Unfortunately many of the best previously sampled wells had been closed and the final wells sampled were not the ideal choices, but a compromise between what was available, the geographic distribution, temperature and depth.

Using silica geothermometry and re-calculating the well concentrations to subsurface aquifer conditions showed that there is little change and no substantial cooling, reheating or dilution of the aquifers in the feed zones surrounding most of the wells sampled. Nevertheless cooling and dilution has occurred in some of the West Rotorua wells since the 1980s. Surprisingly, this appears to be have been caused by dilution of the shallow aquifer fluids with a condensate which appears to be highly enriched with dissolved hydrogen sulphide (H_2S) gas. The concentration of H_2S gas in steam flashed from these well fluids exceeds that of the carbon dioxide gas (CO_2), which has never been observed at Rotorua or any other New Zealand geothermal field.

The slower acting Sodium-Potassium geothermometer, which indicates equilibrium conditions at some distance from the producing wells have increased between $10^{o}C$ to $16^{o}C$ for many of the wells, indicative of a relatively minor increase in source fluid temperatures in the deep aquifer.

Three upflow zones at Kuirau Park, Ngapuna and Whakarewarewa have been previously identified through gas correlations. Based on this very limited dataset, there is a suggestion that the "upflow" may now cover a wider and more diffuse geographic area.

1.0   INTRODUCTION

In Part 1 of this study a geochemical survey of 31 selected natural features in the Rotorua Geothermal Field was undertaken to asses the recovery of springs across the geothermal system following the enforced bore closure programme which began in 1986 (Mroczek et al., 2002). The natural features study showed that the geothermal field in the Kuirau Park – Ohinemutu area was near full recovery while at Whakarewarewa area the changes ranged from aquifer re-heating to continuing decline. In the Ngapuna – Government Gardens the apparent recovery suggested by increases in heat and spring activity were not reflected in the fluid compositions. The main conclusions of Part 1 were that the relative changes in composition of non-reactive and reactive species indicated a greater proportion of deeper aquifer, and hence hotter, fluids were now being discharged at the surface. However, the chemistry of the deep source fluids feeding the shallow aquifers of the geothermal systems was essentially unchanged. A possibility of fundamental change in the underlying fluid compositions as a consequence of an input of heat at depth was suggested by mathematical modelling of the water level rises across the geothermal field (Kissling, 2000).

We continue the study in Part 2 with a geochemical survey of selected Rotorua wells because determination of aquifer relationships and reservoir characteristics solely from spring compositions can be problematic. This is due to the possibility that the spring chemistry may have been altered by low temperature reactions and in particular the difficulty of inferring the degree (and order) of boiling and dilution, and hence the proportion of the thermal end member (Fournier, 1991). In contrast, well fluid and gas compositions from deeper aquifers tapped by wells are generally preferable, as they are less affected by these secondary processes.

In this study we report the chemical and isotopic analyses of steam and water samples collected from 10 wells (Tables 1, 2 and 3) and compare these analyses with historical data. Nearby similar, "proxy" wells have also been included in the dataset due to the paucity of previous data from some of the wells sampled.

The background to this study and project brief are given in Part 1 and are not repeated here (Mroczek et al., 2002).

2.0   SAMPLING PROGRAMME AND ANALYSIS

The locations of the ten sampled wells are listed in Table 1 and plotted in Figure 1. As in the spring study (Part 1), the approach was to choose representative wells to give wide geographical coverage over the entire Rotorua geothermal field. Initially, a selection was made on the basis of availability of previous analyses and high aquifer temperature at depth ("hottest and deepest"), as these well fluids were less likely to be affected by shallow reservoir processes and to be more representative of the deeper aquifer. Unfortunately many of the previously sampled hotter wells are now not available for sampling, having been closed. The remaining wells on the list were inspected and more wells were discounted as poor maintenance made sampling impossible or unsafe. The final wells sampled were not the ideal choices, but a compromise between what was available, the geographic distribution, temperature and depth.

The separated water and steam samples were collected using a Webre Separator to accepted standards for geothermal fluids (Klyen, 1996). Sampling the wells at low pressure and consequently low flow was difficult and time consuming. Wells RR913 and 1016 cycled, and discharged alternating slugs of water and steam during sample collection.

Water samples were analysed to the New Zealand Code of Laboratory Management Practise (NZS/ISO/IEC 17205). The geothermal waters and gases were analysed following the methods laid out in Giggenbach and Goguel (1989).

Oxygen-18 (^{18}O) concentrations were determined by stable isotope mass spectrometry following the methodology of Brenninkmeijer et al., (1987), which was also extended to deuterium measurements (^{2}H).

The analytical data from the 10 sampled wells is presented in Tables 2 and 3. All water samples gave acceptable ion balances ($< \pm5\%$), except that there were unusual interferences which made some of the water samples difficult to analyse. It was suggested that the chemical used to inhibit calcite deposition may have been responsible, but this was not investigated further. Also, when emptied, some of the steam samples had a strong odour of hydrocarbon ("diesel"), whether natural or due to contamination of the aquifer is unknown.

Figure 1.   Location map of wells sampled and proxy wells; compiled by Gareth Evans (Environment Bay of Plenty).

3.0   TREATMENT OF CHEMICAL DATA

3.1   Introduction

Reservoir processes such by cooling, mixing of different production zones, boiling, reinjection returns and cool groundwater inflows cause changes temporally and spatially across the Rotorua Geothermal Field. The following techniques and resultant plots are used in this report to compare the present and historical data.

3.2   Chloride-enthalpy diagram

Changes due to aquifer boiling, mixing (dilution) and conductive heat gain or loss may be identified on a Chloride-Enthalpy diagram (Figure 2). Both components are essentially conservative. The aquifer enthalpy (H) is derived from the inferred aquifer temperature, which is calculated using either the quartz or cristobalite silica geothermometer. In the absence of recent physical well enthalpy or down-hole temperature measurements, the silica geothermometer temperature has been assumed to best represent the temperature in the reservoir in the immediate vicinity of the well. It has also been assumed there is no excess steam in the reservoir, so that the aquifer chloride (Cl_{res}) is the same as the total discharge (TD) composition; i.e. combined steam and water discharged at the wellhead. Renormalising concentrations to total discharge is a convenient method for comparing samples collected at different separation pressures.

Quartz typically controls the silica concentration in reservoir fluids in the Taupo Volcanic Zone and the silica solubility in wells RR889 and M25 appears to be controlled by this silica polymorph. However cristobalite appears to be the controlling silica mineral in the reservoir for the remainder of the Rotorua wells sampled in this study. Figure 2 was constructed by assuming quartz geothermometer for M25 and RR889 and the cristobalite geothermometer for all other wells sampled. This choice of geothermometer was based on the best matches with previously measured down-hole well temperatures (Table 1).

The features of the Chloride-Enthalpy diagram are that H and Cl_{res} both decrease with dilution while H decreases and $Cl_{res,}$ increases with adiabatic cooling (boiling), see Figure 2. The composition of the parent water may be obtained from an intersection of the dilution and boiling lines. There are two dilution lines drawn in Figure 2, dilution of the "parent" type fluids (represented by M25) by a "hot"

low chloride fluid and then a dilution of the cooler reservoir fluids by cold groundwater (Glover and Mroczek, 1998).

3.3 Geothermometers

Three geothermometers, silica (quartz and cristobalite), sodium/potassium (Na-K) and potassium/magnesium (K-Mg) are used to determine subsurface fluid temperatures. The silica geothermometer equilibrates rather quickly so that the corresponding temperatures reflect those at or near the feed points of the wells. The Na-K geothermometer equilibrates slowly so that the temperatures may therefore indicate equilibrium conditions at some distance from the producing wells where waters may reside for very long periods of time. The K-Mg geothermometer is based on mineral reactions which respond faster than for Na-K so that the calculated temperatures reflect the most recent equilibration of the fluids in the shallow aquifer.

Another useful and important geothermometer is the sodium/potassium/calcium, but given the propensity for calcite deposition and current use of inhibitors to suppress scaling, it is considered that the historical data may not be reliable and this geothermometer is not used. Geothermometers were briefly discussed in Part 1 (Mroczek et al., 2002).

3.4 Triangular diagrams

Changes in the relative concentrations of both chemically inert non-reactive species and chemically reactive species using triangular diagrams are used to compare the present and historical well data (Giggenbach; 1991, Mroczek et al., (2002)). For waters the relative proportions of boron (B) – chloride (Cl)- sulphate (SO_4), bicarbonate (HCO_3)- Cl – B, sodium (Na) – potassium (K) – magnesium (Mg) are used.

Relative proportions of the inert and reactive gases are also useful for interpreting reservoir processes. The argon (Ar) – nitrogen (N_2) - helium (He) diagram is useful for classification of gas samples in terms of their likely source and for weeding out samples affected by air contamination (Giggenbach , 1991). The carbon dioxide (CO_2) – hydrogen sulphide (H_2S) - methane (CH_4) diagram reveals boiling processes as there is a marked difference in solubility between methane and the other two gases (helium could also be substituted for methane) so with progressive boiling the residual fluid becomes enriched with the more soluble gases (Giggenbach and Glover, 1992).

3.5 CO₂ in Total Discharge and CO₂/H₂S

CO_2 in total discharge, CO_2 (TD), may be used to indicate whether increases and decreases in the CO_2 concentrations are due to the addition or loss of steam after the liquid equilibrates with cristobalite (or quartz in the case of well RR889). Changes in CO_2/H_2S ratios can be used to suggest possible sources of steam.

3.6 Stable isotopes

Stable isotopes (^{2}H and ^{18}O) are valuable tools for characterising boiling and mixing processes when complemented by and combined with chemical techniques.

4.0 COMPARISON OF RECENT CHEMICAL ANALYSES WITH HISTORICAL DATA

4.1 Data used

The dataset in this study is considerably reduced from the previous study of the natural features. There are relatively few historical samples to compare with the present results, and most of the previous samples were collected between 1983 and 1990. Unfortunately previous analytical data, especially for isotopes, is lacking and two wells, RR741 and 1016, appear not to have been previously sampled. In view of the paucity of data nearby similar, "proxy" wells have been included in the dataset and are also shown in the figures and tables.

The analytical data was abstracted from compilations given by Mahon et al., (1985), Giggenbach and Glover (1992), Stewart et al., (1992), Glover and Mroczek (1998) and unpublished data held in GNS files. The earliest collection date for this set is 1983. Although Glover (1967) undertook an analytical survey between 1961 and 1963, which included many wells, none overlap with the present survey.

Table 1 lists other important information on the wells; the drilled and cased depths, discharge enthalpy and corresponding enthalpy temperature (assuming vapour saturated liquid water) and maximum downhole temperature. This data was abstracted from Environment Bay of Plenty and GNS files and was most likely originally compiled during the Rotorua Task Force investigations in the early 1980s (Mahon et al., 1985). Also included in Table 1 are the silica geothermometer temperatures for the recently sampled wells and the typical silica geothermometer temperature for the proxy wells.

Tables 4 and 5 list the historical and recent water and steam compositions respectively. Table 6 shows steam compositions on dry gas basis. This renormalisation is particularly useful when comparing steam samples as concentrations, expressed in the standard units of moles of gas per 100 moles of steam, can vary enormously with small changes in the degree of flash for the low pressure Rotorua wells. Table 7 lists the compositions of only the proxy wells.

In Table 1 the wells sampled are conveniently grouped into four regions of the geothermal field; viz. Kuirau Park (NW), Government Gardens (NE), Ngapuna (E) and Western Rotorua. Unfortunately there were no suitable wells to sample in the southern part of the field close to Whakarewarewa.

In the following sections we discuss the historic data and how the new data relates to these.

4.2   Chloride-enthalpy diagram

The chloride-enthalpy diagram for the sampled and associated proxy wells is shown in Figure 2. The data used to construct the diagram are given in Table 8. In understanding the changes in this (and subsequent other plots) it is more important to consider overall trends and not to over interpret relatively small absolute changes in reservoir enthalpy (H) or reservoir chloride (Cl_{res}). For an appreciation of the variability in the earlier results consider the three samples (1 weirbox and 2 webre) collected from well RR913 on 27/5/86; all have a Cl_{res} of about 285 mg/L but the H for the three samples varies between 705 and 743 kJ/kg. This is equivalent to silica geothermometer temperatures between 167 and 175$^{\rm o}$C. There is a ±5% uncertainly in the silica analysis which equates to about ±3$^{\rm o}$C in the silica geothermometer temperature.

Similarly for well RR889 a weirbox and a webre sample were collected on 27/7/89 and have H of 950 kJ/kg and 933 kJ/kg respectively (=3°C difference in silica temperature) but a Cl_{res} of 1425 and 1370 mg/L respectively. The uncertainty in the chloride is ± 35 mg/L so the results may be just within the errors and both samples had acceptable ion balances. However as other components in the weirbox sample also seem elevated compared to the webre sample (and other samples), an artefact of sampling or sampling errors may have affected it.

There are two clusters of points on the Chloride-Enthalpy diagram in Figure 2, the high chloride – high enthalpy "parent" fluids represented by wells M25 and RR889 and the rest of the cooler diluted fluid sampled in the remaining wells. Although there are changes in the reservoir chloride and enthalpy, they are not large and the historical and recent data tend to plot in the same portions of the Chloride-Enthalpy diagram. This suggests that there is little change and no **substantial** cooling, reheating or dilution of the aquifers in the feed zones surrounding the wells. Nevertheless there are decreases in both H and Cl_{res}, mainly in the West Rotorua wells, since the 1980s. This is surprising and appears to be caused by dilution of the shallow aquifer fluids, which these wells tap, by a gas-rich condensate.
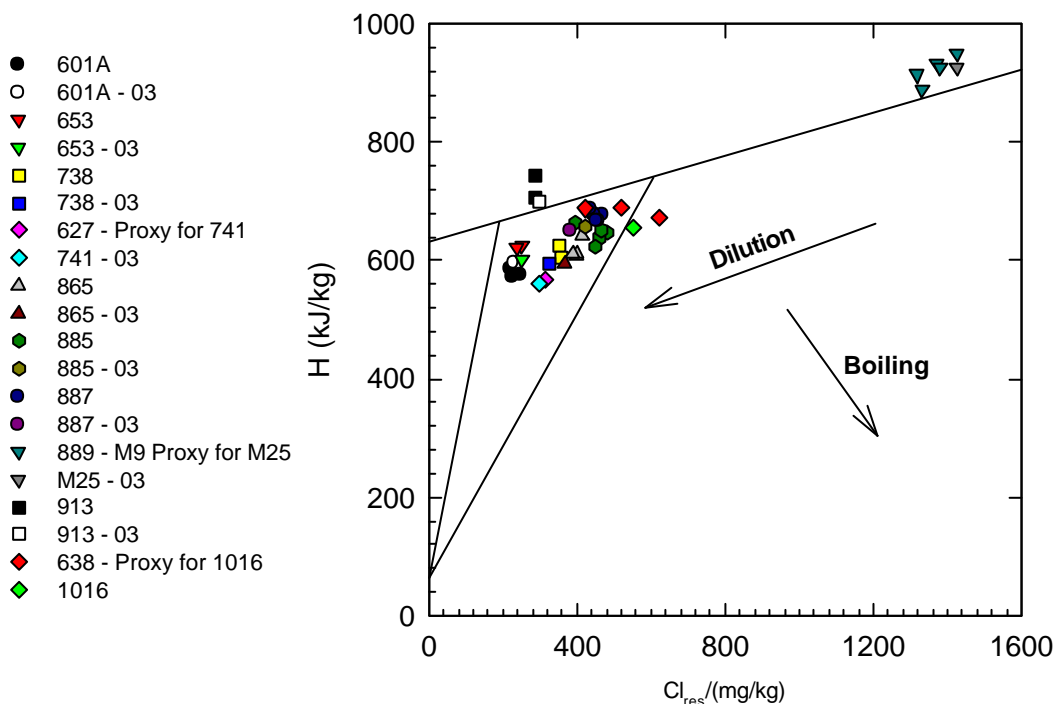
Figure 2. Chloride-Enthalpy diagram for the sampled and proxy wells.
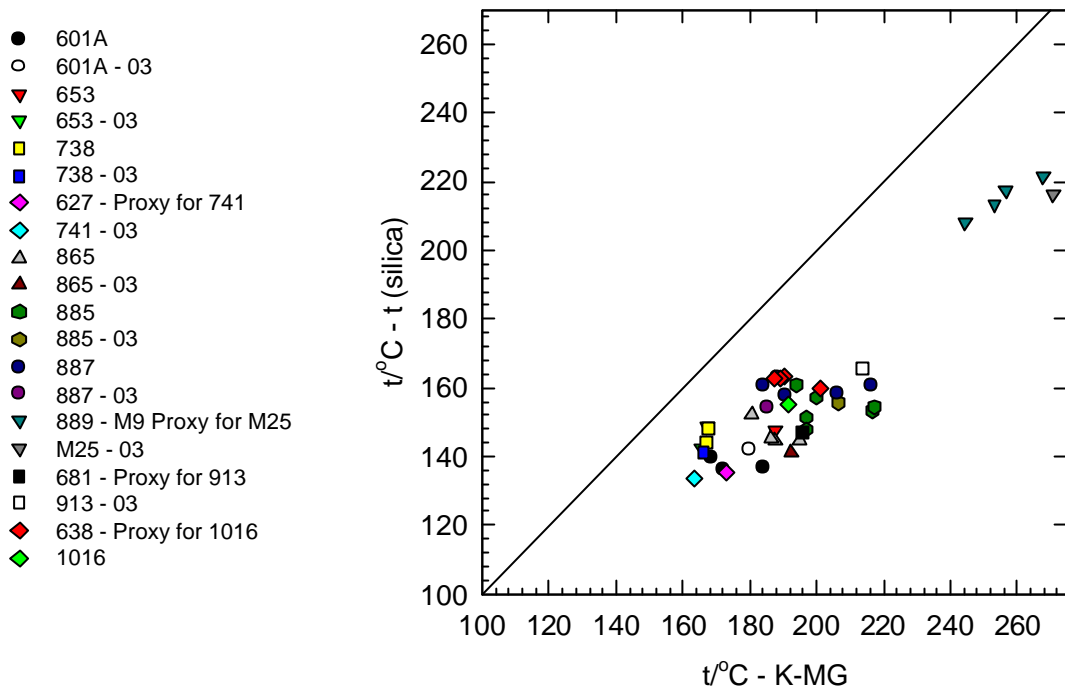
Figure 3. Silica geothermometer vs K-MG (Giggenbach) geothermometer. a-Cristobalite solubility was assumed to determine the concentration of dissolved silica in all wells except for M25 and RR889 where the fluids were assumed to be in equilibrium with quartz.
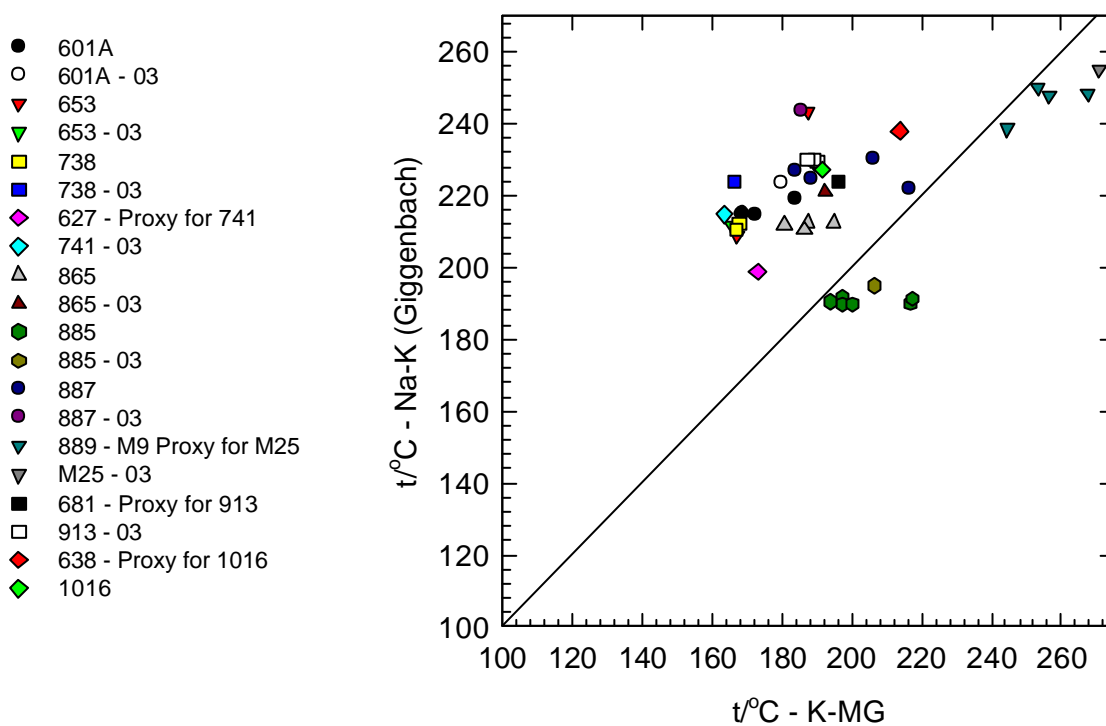
Figure 4. Na-K (Giggenbach) geothermometer vs. K-MG (Giggenbach) geothermometer.
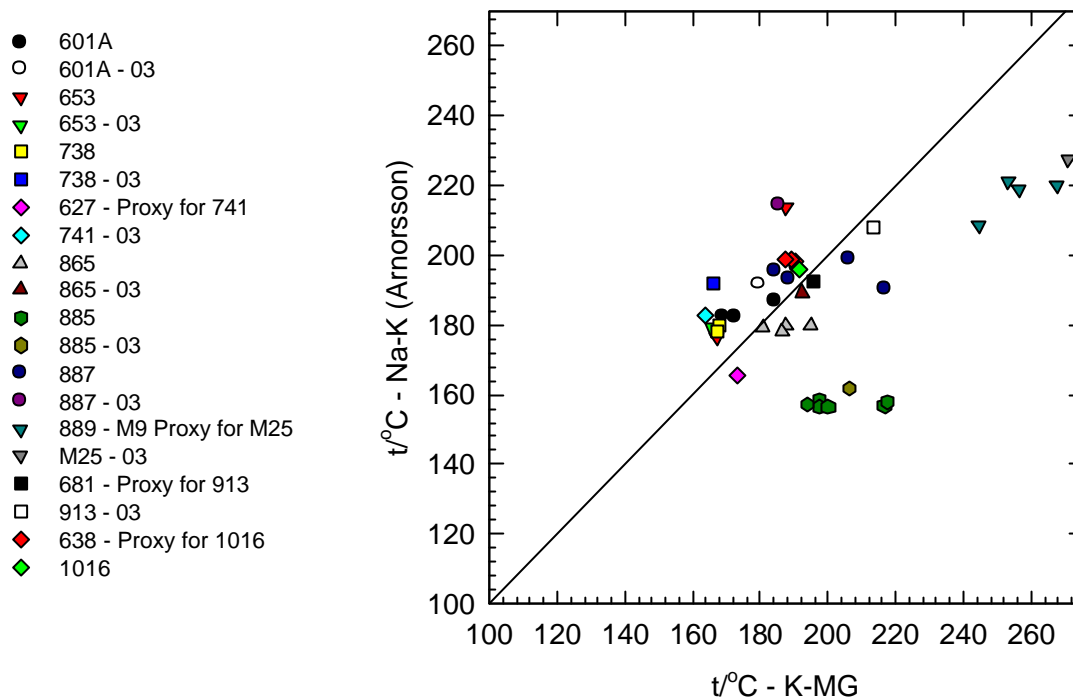
Figure 5.   Na-K (Arnórsson) geothermometer vs. K-MG (Giggenbach) geothermometer.
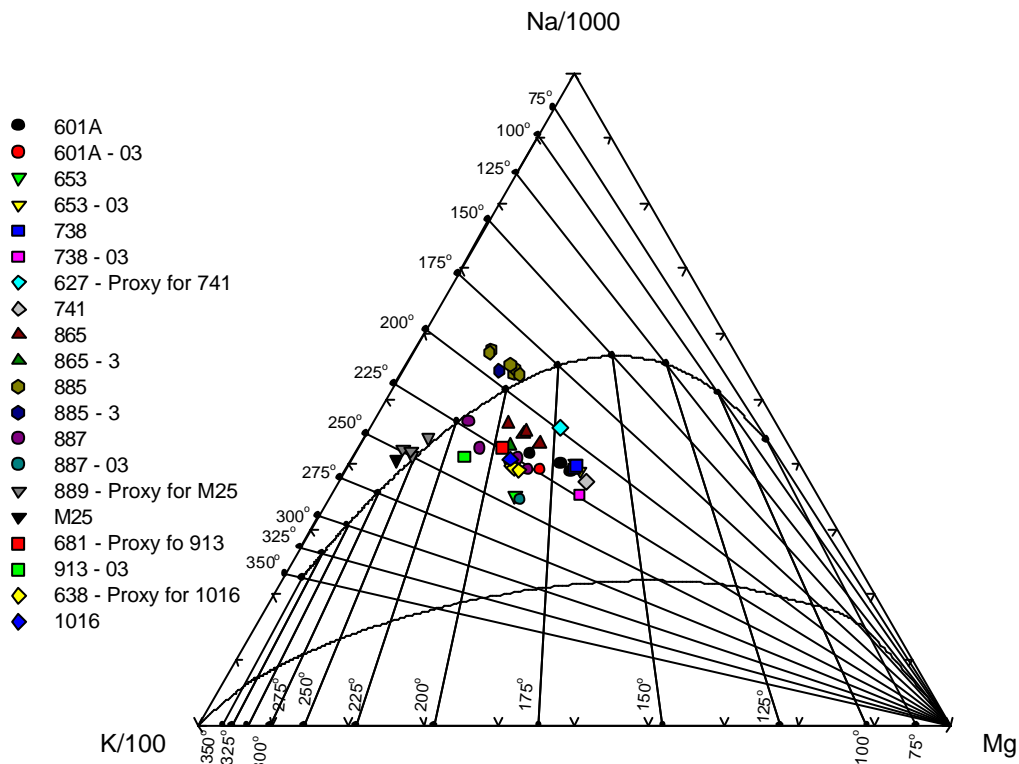
Figure 6.   K-Na-Mg ternary diagram for evaluating Na-K (Giggenbach) and K-MG
(Giggenbach) geothermometer temperatures.

4.3   Silica, Na-K and K-Mg geothermometer correlations

Figures 3 to 5 show the temperature dependence of these three geothermometers.   If the fluids were in full equilibrium then the different geothermometers should give correspondingly similar temperatures and lie along the full equilibrium line. Figure 3 shows that fastest acting silica geothermometer gives lower temperatures (~40°C) than indicated by the slower acting K-Mg geothermometer.   Similarly in Figure 4 the slower acting Na-K geothermometer is higher by about 30°C than the faster acting K-Mg geothermometer except there appears to be better agreement with well RR885 and the hottest well RR889. Close agreement can be expected between the fast and slower acting geothermometers if all fluids were at similar temperatures for long periods of time. Other effects that could cause an apparent change in geothermometer temperature include removal of Mg in clays and silica during boiling (Giggenbach and Glover 1992).

In Part 1 it was briefly stated that application and interpretation of the cation geothermometers is not a trivial task (Mroczek et al., 2000). Arnórsson's (2000) Na-K geothermometer formulation gives much better agreement (Figure 5) with the K-Mg geothermometer except for wells RR885 and RR889. Figure 6 is the ternary K-Na-Mg ternary diagram used for evaluating Na-K and K-Mg geothermometer temperatures and this is the same data which was presented in orthogonal form in Figure 4. Figure 6 clearly shows the high temperature of the M25/RR889 fluids, which lie on the full equilibrium line, separated from the remaining cooler fluids.

It is important to note that equations for the cation geothermometers are based on concentration ratios, so that neither boiling nor dilution (with low mineralized fluid) alters the derived temperature, despite affecting the absolute concentrations.

For many of the recently collected samples the derived K-Mg geothermometer temperatures are unchanged since the 1980s while the Na-K temperatures have increased by up to 16°C, indicative of an increase in source fluid temperatures in the deep aquifer.

4.4 B, Cl, SO$_4$ and HCO$_3$ correlations

In Figures 7 and 8 the relative proportions of these anions show intermediate and shallow depth aquifer processes. Previous work (Glover, 1967; Giggenbach and Glover, 1992; Stewart et al. 1992) showed that the geothermal waters could be split into two groups on the basis of their locations and chloride/bicarbonate ratios. The east and south group waters (ES) are mainly or entirely resident in Mamaku Ignimbrite and have high chloride concentrations relative to bicarbonate; ratios are often 10 (by weight) or more. The north and west group waters (NW) are normally resident in Rotorua Rhyolite and have ratios of 1-2. The ratios are significant in terms of the processes which have affected the waters. Both groups are believed to arise from the same deep parent water, but the ES group waters have risen to shallow levels before dilution by groundwater, which allows CO$_2$ to escape from solution because of the lower pressures. In contrast, the NW group waters have been diluted and cooled at deeper levels, causing the trapped (dissolved) CO$_2$ to form bicarbonate by reaction with the rocks. Similarly Glover (1967) showed that Cl/B ratios decrease from about 130 (by weight) in the south at Whakarewarewa to 50 in the north-west. Sulphate (SO$_4$) is formed at shallow levels in the aquifer due to oxidation of H$_2$S.

In reducing the HCO$_3$ data there are two difficulties. The first is differentiating between "true" bicarbonate and "total" bicarbonate (as listed in the analytical tables) and the second is that the present samples were collected at above atmospheric pressure while most of the historical data was collected at atmospheric pressure. To compare like with like the present data was reduced to atmospheric pressure using the computer code WATCH. This made a substantial difference to the amount of bicarbonate in some of the samples due to the flashing off as carbon dioxide gas (CO$_2$), e.g. 600 ppm HCO$_3$ at 4 bg for well 887 was recalculated to be 327 ppm HCO$_3$ at atmospheric pressure. "Total" bicarbonate analyses include all forms of carbonate species; i.e. dissolved CO$_2$, HCO$_3^-$ and CO$_3^=$. However only in RR738 was the residual carbonic acid sufficiently high (35 ppm) to be taken into account (i.e. taken off the "total" bicarbonate value for the sample flashed to atmospheric pressure) in determining the "true" HCO$_3$. As no steam samples were collected from wells RR653 and RR741 due to low wellhead pressures, the relative proportions were as analysed "total" bicarbonate. Any previous samples at above atmospheric pressure were excluded from the comparison. The data used to construct Figure 8 are listed in Table 9.
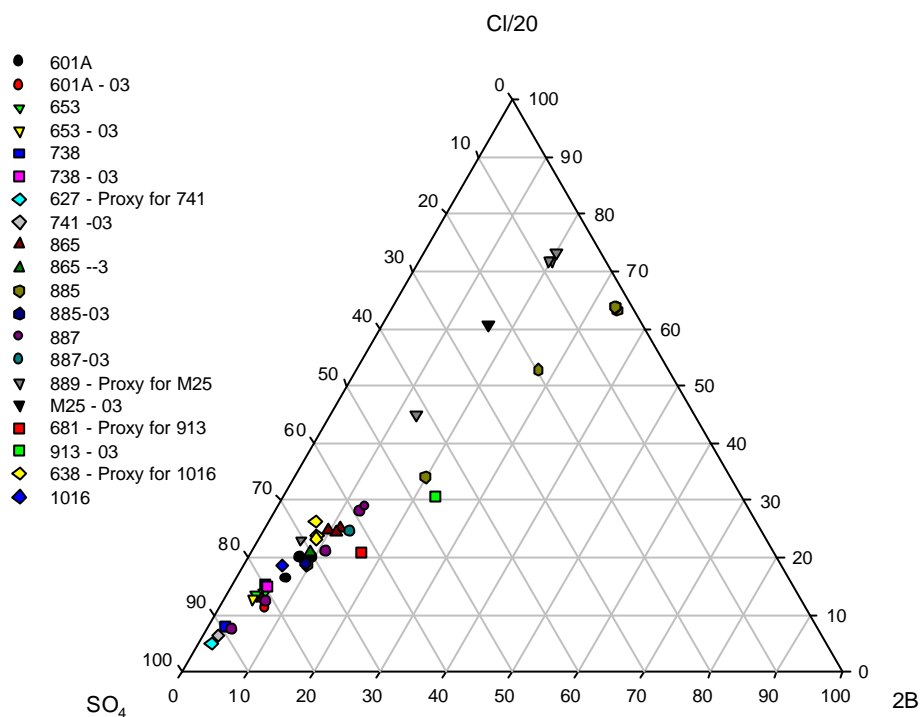
Figure 7.   B-Cl-SO₄ ternary diagram.
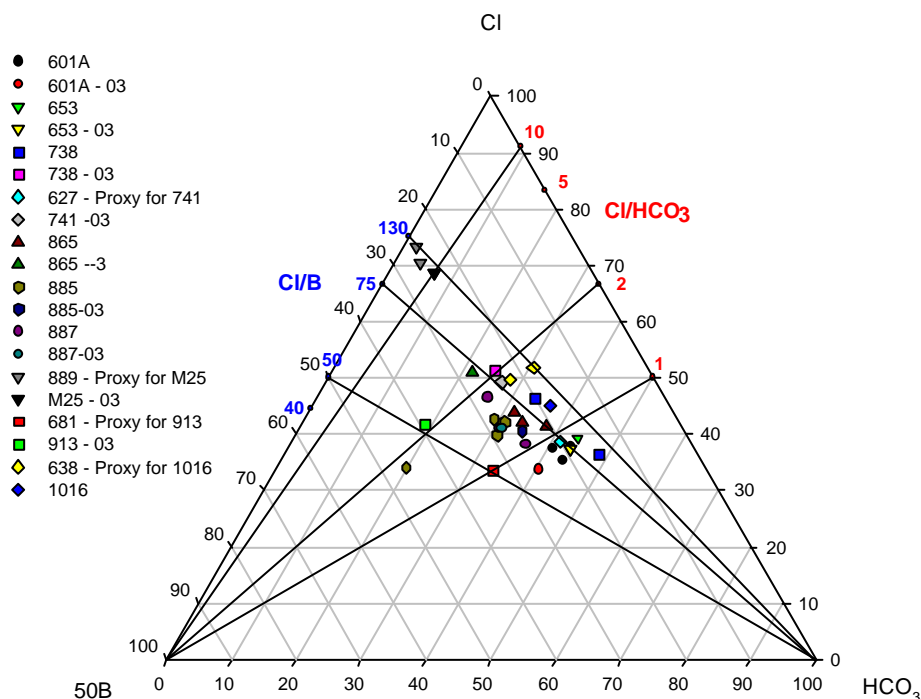
Figure 8.   B-Cl-HCO₃ ternary diagram. The present Kuirau wells, RR913, RR601A and proxy RR681, are all enriched in He and have the similar relative proportions as other Kuirau well and natural features reported by Giggenbach and Glover (1992).

4.5   Comparison of present water results with earlier data

4.5.1   Kuirau - Ohinemutu

RR601A

This well is located immediately south of Kuirau Park near the western side of the Rotorua Field. The well is 173 m deep, cased to 134 m with a maximum temperature of 153°C. There has been a small increase in Cl_{res} and H over the last decade but the fluids are still slightly more dilute than in 1983. Na-K and K-Mg geothermometers temperatures have increased slightly, about 10°C. There is no increase in HCO_3 relative to B and Cl and a small increase in sulphate.

RR913

Well RR913 is located within Kuirau, being drilled to 146.5 m (cased 121 m) with a maximum downhole temperature of 152.5°C. There has been small increase in Cl_{res} compared to samples collected in 1986 and there is essentially no change in H. This well alternates as a reinjection/production well for the Aquatic Centre but there appears not to have been any significant cooling effect on the aquifer. There are no previous RR913 samples with K analyses, but in the present sample temperatures are higher by about 16°C than the nearby proxy well RR681 sampled in 1984. The Cl/HCO_3 ratio has halved (2.2 to 1.2) compared to a RR913 sample collected in 1986 (not included in the plots as B missing). The Cl/HCO_3 ratio in the proxy well RR681 is about 1.

Little change in the conservative components suggest that the shallow aquifer is similar to that present in the 1980s, expect there is an indication of higher temperature source fluids.

4.5.2   Government Gardens

RR885

Well RR885 is located in the northern part of the Garden, near Rachel Spring. It is drilled to 112 m, cased to 68 m. The maximum downhole temperature is 161°C. The 2003 samples are essentially similar in composition to samples collected in 1984-1990. There is some variability, in Cl_{res}, e.g. higher by 30 mg/L than in 1990 but lower by 20 mg/L than in the sample collected in 1989. Only a very small increase in cation geothermometer temperatures (5°C). There is also a small increase in

relative amounts of HCO_3-Cl-B. Compared to the sample collected in 1990, there is an increase in sulphate but the sample is very similar to that collected in 1989.

RR887

This well is located to the southeast, near the lake and Sulphur Bay. It is drilled to 107m, being cased to 96 m with a maximum temperature of 149^oC. There is only a slight decrease in H, but a significant decrease in Cl_{res} compared to samples collected in 1984-89. The difference between the Na-K and K-Mg is instructive in the light of this apparent dilution. The K-Mg geothermometer is essentially unchanged from previous samples, at 185^oC for the present analysis, but the Na-K geothermometer has increased by about 14^oC to 244^oC. Thus although the shallow hydrology may have changed with increased dilution, the deep fluid fraction appears to be hotter. The relative proportions of Cl-B-SO_4 are similar to samples collected in 1984-89 but the present sample contains more bicarbonate.

In summary there appears to be a significant change in the shallow hydrology of the field in the vicinity of RR887, while relatively unchanged in the northern part of the Gardens.

4.5.3   Ngapuna

M25

M25 is the replacement well for RR889 (M9) being drilled and cased to 245 m, with a maximum downhole temperature of 211^oC. Giggenbach and Glover (1992) suggested that all Rotorua waters could be derived from one high chloride parent water with a composition close to that tapped by RR889. Ignoring the "anomalous" high chloride weirbox sample discussed above, there has been a small progressive increase in Cl_{res} since 1983 from 1318 mg/L to 1424 mg/L in 2003 but no change in H. Na-K and K-Mg temperatures are essentially unchanged from previous RR889 values (6^oC higher). There now appears to be slightly less bicarbonate in the fluids and slightly more sulphate, but these changes are probably well within the natural variations.

4.5.4   West Rotorua

RR653

This well on the southwestern boundary of the Rotorua Field is drilled to 131 m, and cased to 100 m. A maximum downhole temperature of 141°C is recorded. A small decrease in H (equivalent to 4-7°C) is observed but no change in Cl_{res} since the 1989 sample.   Na-K and K-Mg temperatures are lower than measured in 1990 but similar to 1989. The present sample has similar relative proportions of B-Cl-HCO_3 and B-Cl-SO_4 as previous data.

RR738

RR738 is drilled in the central southern part of the field where the rhyolite domes dominate the subsurface geology. A small decrease in H (equivalent to 3°C) and also in Cl_{res} (33 mg/L) is recorded. As in RR887 where there was also a decrease in Cl_{res}, the Na-K temperature has increased by 13°C while K-Mg is essentially unchanged.   The relative amount of HCO_3 has also decreased.   The absolute concentration (92 mg/L) is lower than for the sample collected in 1990 (211 mg/L) but about the same as in 1989.

RR741

Well RR741 is drilled to 130 m, being cased to 104.4 m. A maximum downhole temperature of 123°C has been recorded. This well is located in the central area of the rhyolite aquifer. Both the H and Cl_{res} (16 mg/L lower) are similar as the nearby proxy well RR627 sampled in 1984.   Na-K temperatures are higher by 16°C, while K-Mg are similar. The relative proportion of HCO_3 is much lower than in RR627.

RR865

This well is drilled to 105 m (cased to 89.5) with a maximum recorded downhole temperature of 130°C. It is in the central area of the rhyolite aquifers. There is a small decrease in H (equivalent to 3°C) and also in Cl_{res} (23 mg/L), compared to previous samples. Na-K temperature is higher by 11°C and K-Mg is similar to previous values. The relative amount of HCO_3 is lower compared to previous values.

1016

Well 1016 is drilled to 120 m (cased to 91 m) with a maximum downhole temperature of 135°C. Well 1016 is slightly cooler than the nearby proxy well RR638 (~8°C) but is less dilute. The Cl$_{res}$ of 130 mg/L is higher than the RR638 samples collected in 1990, but only 22 mg/L higher than in 1989. Cation geothermometer temperatures are similar to RR638.   This fluid contains much higher bicarbonate than the nearby proxy well RR638, but a similar proportion of sulphate. Large swings in concentration such as between the 1989 and 1990 samples observed in RR638 (and others discussed above) may reflect local exploitation induced effects.

In summary there appears be a decrease in H and Cl$_{res}$, in the shallow aquifer fluids feeding these central wells, while the Na-K temperatures have increased.

4.6   Comparison of present gas results with earlier data

Steam sampling was undertaken so that detailed gas analyses could be conducted. However the comparison of gas results is restricted due to the paucity of previous data. Tables 5 and 6 list the previous and recent data. The latter table, which list the gas concentrations on a dry gas basis, is best for comparing results as it eliminates the artefact of varying flash fractions in these low pressure wells. Giggenbach and Glover (1992) is the only published study to have interpreted the chemistry of the gas discharges and this was based on one limited data set collected in 1989.

4.6.1   Ar-N$_2$-He

Based on the relative proportions of argon (Ar), nitrogen (N$_2$) and helium (He) Giggenbach and Glover (1992) identified three upflow zones; Kuirau Park, Ngapuna and Whakarewarewa. The gases most highly enriched in He were from Ngapuna. However well RR889 (M9) did not fit this pattern and was found to be in the group most depleted in He and containing a high proportion of atmospheric gases (see their Figure 7, Giggenbach and Glover; 1992). Figure 10 show that the present M25 value now plots well into the He enriched field, suggesting that the previous RR889 results was either in error or as suggested by Giggenbach and Glover subject to secondary exploitation induced processes.
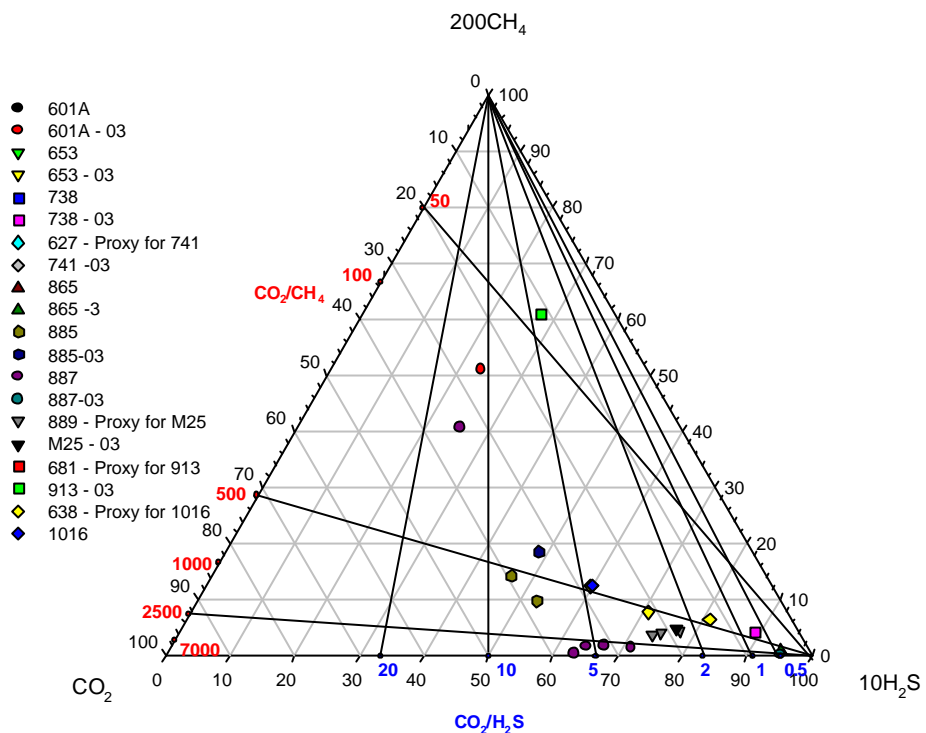
Figure 9. H_2S-CH_4-CO_2 ternary diagram.
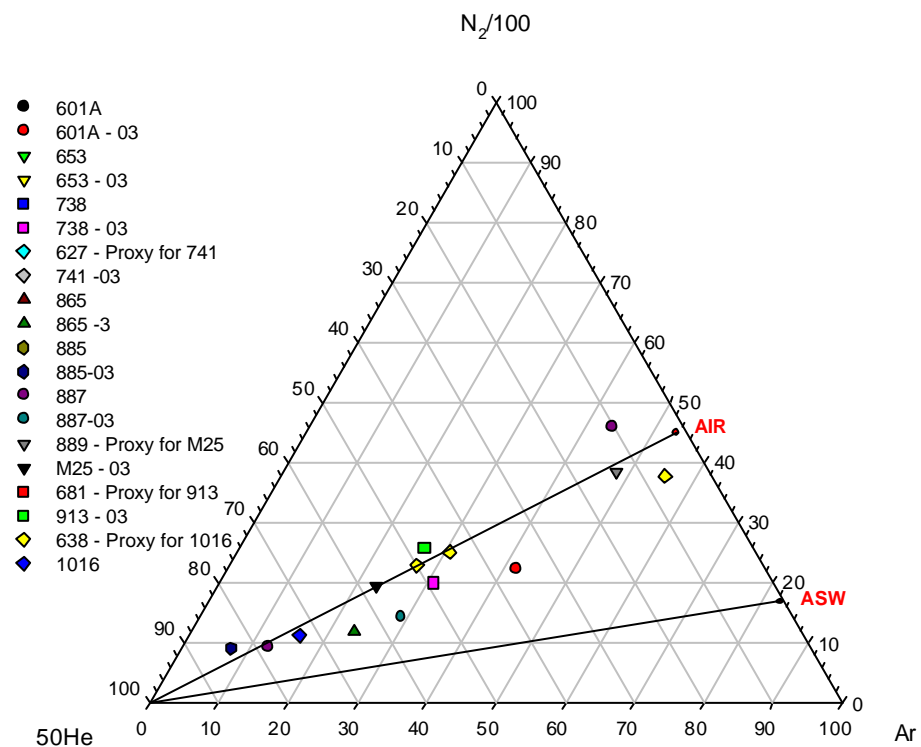
Figure 10. Ar-N_2-He ternary diagram.

Of interest is the very high He enrichment to the North East, particularly RR885, which is similar to the Ngapuna features reported by Giggenbach and Glover (1992) but also in RR887. Two previous samples exist for RR887, one enriched in He and the other contaminated with air so perhaps this area was always enriched with He. Giggenbach and Glover (1992) sampled well RR877 ("Polynesian Pool"), but this sample is highly depleted in helium and plots near the relative proportions of air, unlike RR887 the (114 mE of RR877) 2003 sample.

Also of interest is the high relative enrichment in He for the Western bores for which samples could be collected. In particular 1016 and RR865 are more enriched in He than Kuirau or Whakarewarewa features but similar to Ngapuna, as reported by Giggenbach and Glover (1992). RR638, the proxy well for 1016, is less enriched but still lies in the same 'Kuirau' region of the diagram as does RR738.

Based on this very limited dataset, there is a suggestion that the "upflow" zones identified through enrichment of He relative to Ar and N_2 may cover a wider and more diffuse geographic area than identified previously.

4.6.2 H_2S-CH_4-CO_2

This correlation was used by Giggenbach and Glover (1992) to show that fluids over the eastern part of the field are degassed with respect to methane (CH_4), due to boiling in the inferred upflow zone. Equilibration of the gases at high temperatures, which could also explain the relative loss of the sparingly soluble CH_4, was discounted as there was no shift observed towards the CO_2 apex of the diagram. H_2S is considerably more soluble than CO_2 so that boiling results in a relative decrease in CH_4 and an increase in H_2S. In contrast at Kuirau the fluids ascend without boiling and the gases remain relatively enriched in CH_4.

As shown in Figure 9, the present data fits in with the trends identified by Giggenbach and Glover (1992). The Kuirau samples from Wells RR913 and RR601A are relatively enriched in CH_4 (CO_2/CH_4 ˜ 50), while Ngapuna well M25 is depleted in CH_4 (CO_2/CH_4 ˜ 1000). Wells with intermediate ratio (CO_2/CH_4 ˜ 500), include the Western wells, RR885, RR738 and 1016 (and proxy 638) but all are variably enriched in H_2S, RR738 being highly enriched in H_2S. Except for one obvious outlier, the historical samples for RR887 are the most depleted in CH_4 (CO_2/CH_4 ˜ 2500). In contrast the present RR887 sample is even more depleted with respect to CH_4 (CO_2/CH_4 ˜

3800) and is significantly more enriched in H_2S. The same applies for sample RR865 but no earlier analyses exist with which to compare.

4.6.3 CO_2(TD) and CO_2/H_2S

Steam samples from wells RR738, RR865 and RR887 have CO_2/H_2S ratios of 0.74, 0.45 and 0.50 respectively. This is an extraordinary result and as far as we are aware this is the only case recorded where the H_2S concentration exceeds the CO_2 in steam from a geothermal well in New Zealand (or elsewhere). These three wells are all producing slightly cooler and more dilute fluids, which perhaps suggest mixing with H_2S enriched end-member fluid. Boiling at depth with phase separation and subsequent condensation of steam in which gas dissolves at shallow levels could form such a fluid as the most soluble gas, H_2S, accumulates preferentially with depletion of the less soluble gasses. There was no significant change in SO_4 in the fluids suggesting the parent mixing fluid is not percolating down from the aerated groundwater table. Modelling may be able to determine a viable formation mechanism. Their extent, range and depth of the H_2S enriched fluids, roughly lying NW-NE and centred on RR865, are unknown. They were not observed further East in Well RR653, immediately to the south at well 1016 or further north at well RR885.

Webre sampling cannot give rise to such an unusual CO_2/H_2S ratio and also deplete the gas in CH_4. One of the wells, RR887, was sampled at good pressure (4 bg) and flows which tends to discount other possible low pressure sampling artefacts. The very high H_2S in steam (and as a consequence also in the separated water) was noted at the time of analysis but the lab notebooks were rechecked to ensure there were no errors in methods, transposition or calculation. The evidence is that these are valid but highly unusual gas samples. Further sampling of some of these wells (e.g. RR887) has taken place as part of the hazards monitoring GEONET programme, but are not yet analysed. An analysis of these samples will enable a confirmation of the present results.

The CO_2 in total discharge vs CO_2/H_2S is shown in Figure 11. A plot of this type can be used to determine whether the changes in CO_2 concentrations are due to the addition or loss of steam and also to suggest possible sources of steam. The accuracy is dependent on reliable enthalpy data to calculate the gas in the total discharge, which unfortunately is not available for any of the wells sampled.   When a fluid boils progressively the CO_2 and CO_2/H_2S in the residual fluid decreases, but the ratio does not decrease as rapidly as the CO_2 due to the higher solubility of H_2S.   It is clear from the plot that the highest CO_2 (TD) for well RR738 and also the hottest "parent like" M25 cannot

account for the variation in gas concentration across the field by simple boiling, pointing to complex shallow aquifer processes such as the conversion of CO_2 gas to HCO_3 in the east through water-rock reaction, as previously discussed, and also now the apparent mixing of H_2S rich condensates.
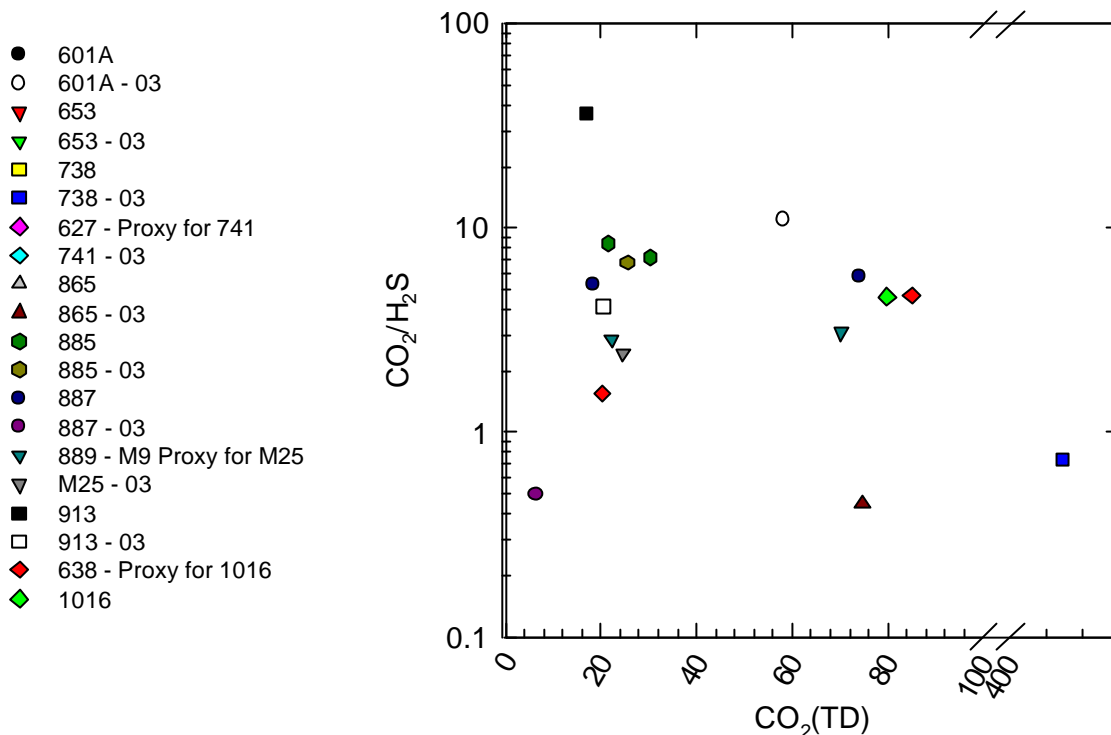
Figure 11. CO_2 in Total Discharge vs CO_2/H_2S.

5.0 COMPARISON OF ISOTOPIC ANALYSES WITH HISTORICAL DATA FOR ROTORUA GEOTHERMAL WELLS

Results of isotopic measurements for geothermal bores sampled in 2003 are given in the Table 10 with earlier measurements from the same or similar nearby bores (Stewart et al. 1992). The isotopic concentrations are expressed as d values with respect to a water standard (V-SMOW), i.e. $d^{18}O = [(^{18}O/^{16}O)_{sample}/(^{18}O/^{16}O)_{SMOW} - 1]$ x 1000.

d^2H is defined similarly. Chloride and bicarbonate concentrations are also given.

The data are plotted in Figures 12-15. As discussed above the geothermal waters can be split into two groups on the basis of their locations and chloride/bicarbonate ratios; the east and south group waters (ES) are mainly or entirely resident in Mamaku Ignimbrite and the north and west group waters (NW) are normally resident in Rotorua Rhyolite.

In the plots, ES group waters are represented by squares and NW waters by diamonds. The 2003 data are plotted as solid symbols and historical data as open symbols. Figure 12 shows $d^{18}O$ versus d^2H values. Rain waters are expected to plot close to the "meteoric water line" which has been determined from many measurements on New Zealand rainfall. The average composition of groundwater in the Rotorua area is represented by the symbol "G", which plots close to the line as expected. A trend line through the NW group waters extends from the groundwater point to more positive $d^{18}O$ and d^2H values, intercepting a dashed line through the ES group samples. The NW group trend shows the effect of groundwater dilution of deep geothermal water. The dashed line shows the effect of steam separation (boiling) from deep geothermal water as it rises to higher levels and lower pressures. Figure 13 shows d^8O versus chloride concentrations, with the same trend lines.

Figures 14 and 15 show temperature and bicarbonate concentrations versus chloride concentration. The trend line through the NW group waters is curved to meet the groundwater point; this curve represents heat contributed by hot rock (conducted heat) as groundwater within rhyolite aquifers is drawn convectively into the system at depth. The chloride/bicarbonate plot shows the marked difference between the two groups of waters. There is an indication from this plot that the bicarbonate concentrations in the NW group are increasing relative to the chloride concentrations.

5.1   Kuirau Park

Two bores were sampled in the Kuirau Park area. Well RR601A was sampled in July 1983 and Sep 1989, as well as in Jan 2003. The isotopic composition shows very little change over this time (Table 10). No earlier measurements are available for well RR913, but nearby bores (RR619 and 681) showed similar compositions although cooler water in the 1980s. The Kuirau bores continue the observed pattern of relatively dilute chloride-bicarbonate waters for the area, with temperatures perhaps related to proximity to an upflow.
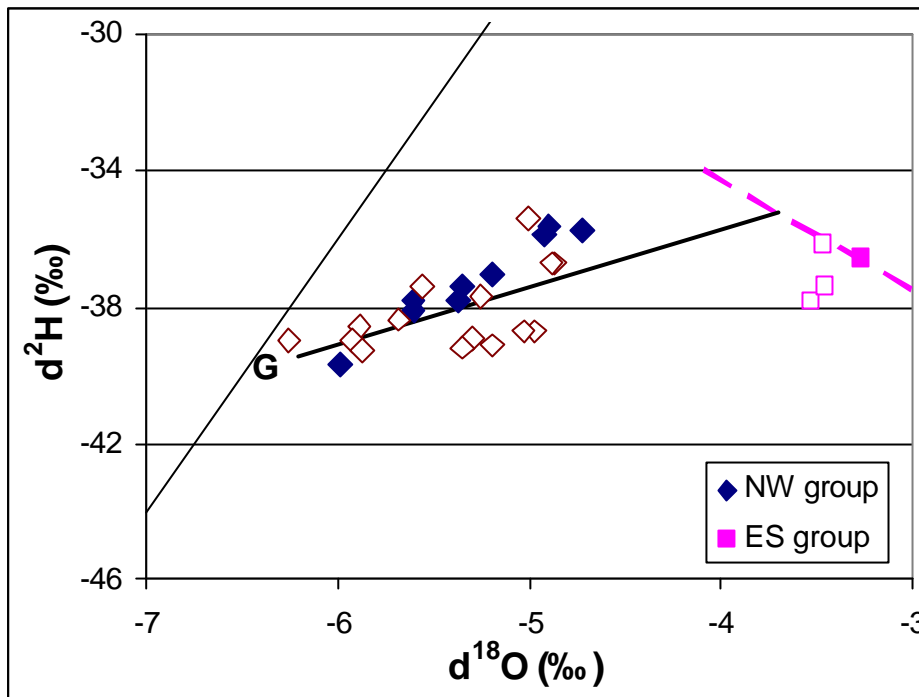
Figure 12.   Plot of d^{18}O versus d^{2}H values for Rotorua geothermal waters.
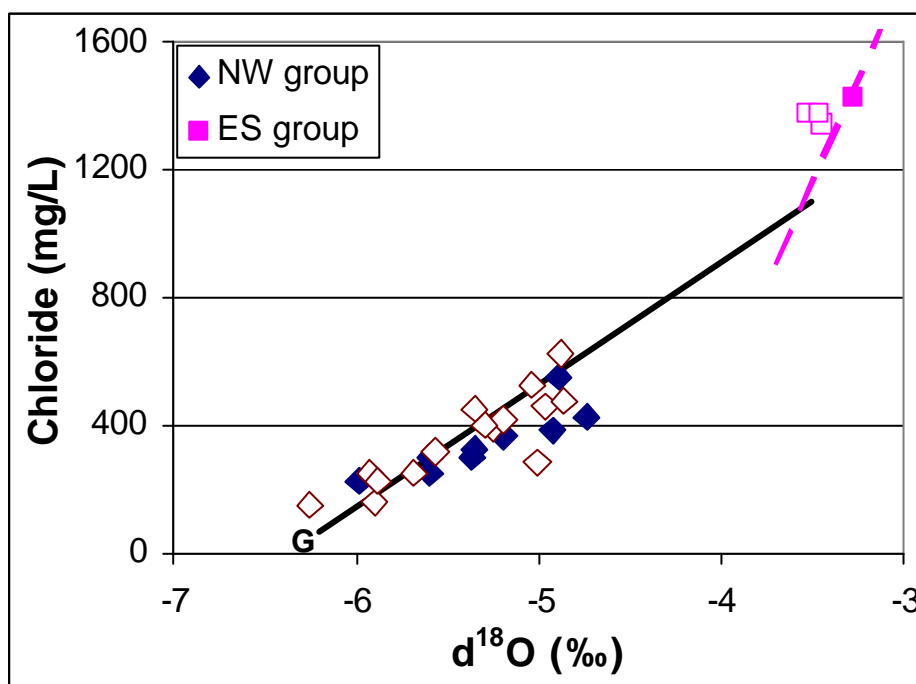
Figure 13.   Plot of d^{18}O versus chloride concentrations for Rotorua geothermal waters.
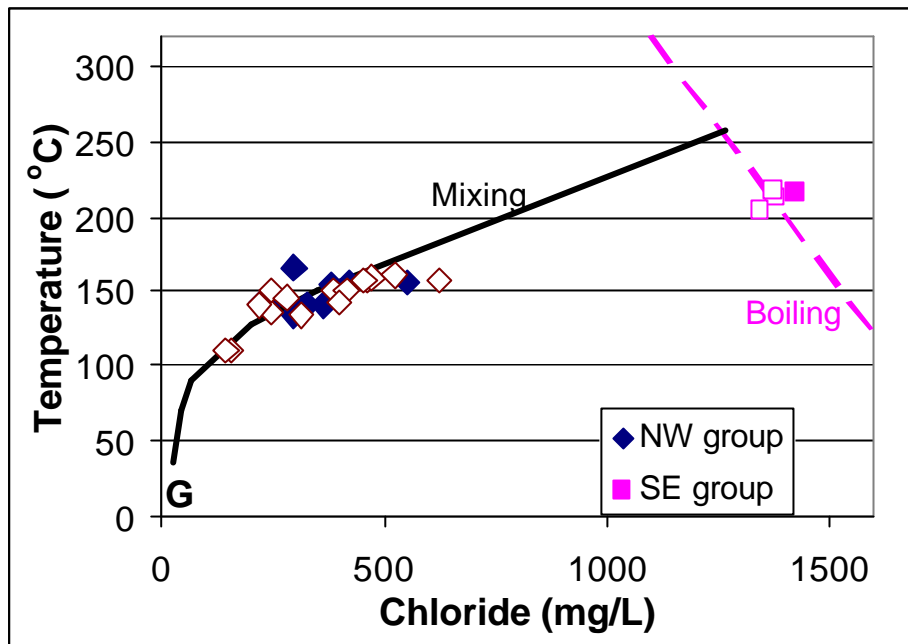
Figure 14. Plot of chloride concentration versus downhole temperatures for Rotorua geothermal waters.
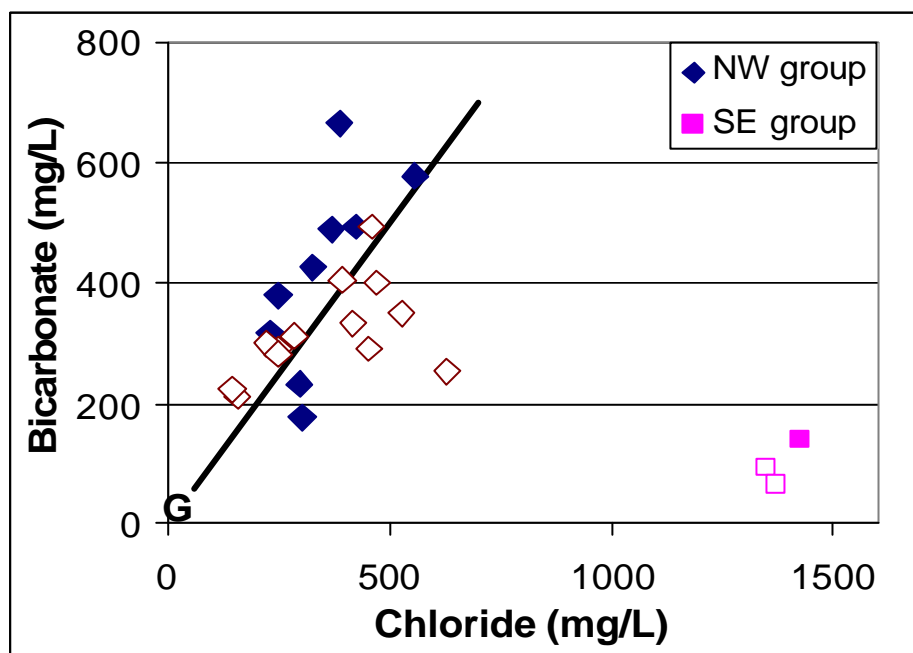
Figure 15. Plot of aquifer chloride concentration versus bicarbonate concentrations for Rotorua geothermal waters.

5.2   Government Gardens

Bores RR885 and 887 are in the high bicarbonate (Government Gardens) region. RR885 has slightly more positive d values than RR680 (sampled in 1989), but the bores have similar temperatures and chloride/bicarbonate concentrations. RR887 was sampled in the 1980s and 2003. The 2003 and 1984 samples are similar, but the 1989 sample again has more negative d values. The 2003 sample has increased bicarbonate and lower chloride, indicating changed flow conditions from depth.

5.3   Ngapuna

M25 is in the Ngapuna area, and is compared with the previously sampled nearby well M9. Both tapped high chloride water, representing the least diluted water in the field. This is the only well from the ES group that was sampled in 2003. M25 has slightly higher $d^{18}O$ and chloride, but it is not possible to say if this represents a significant change in time, or simply reflects stable dilution patterns in the area. The latter is more likely.

5.4   West Rotorua

Five bores were sampled in this area in 2003. The bores (RR653, 738, 741, 865 and 1016) have increasing $d^{18}O$ values, and chloride and bicarbonate concentrations, in this order. Compared with their selected comparison bores, they have similar isotopic and chloride concentrations, but higher bicarbonate concentrations. This would suggests a trend of increasing bicarbonate concentrations in the area, meaning less dilution is occurring of the waters generated deeper in the system by reaction of dissolved CO_2 with rock. However comparison against previously sampled wells, not the isotope proxy wells and reducing the data to atmospheric pressure shows, that for most wells the relative concentrations of bicarbonate are either similar or slightly lower (relative to Cl and B). There is no previous data to compare with well for 1016 where indeed the HCO_3 is much higher than the nearby proxy well. High bicarbonate implies entry of less groundwater from shallow levels from the south (Stewart et al. 1992 demonstrated shallow groundwater entry in this area in the 1980s based on elevated tritium and sulphate concentrations in the waters).

6.0   DISCUSSION

The chemistry of the Rotorua well discharges show that changes are continuing to occur in the hydrology of the geothermal field. Typically there are only relatively minor increases/decreases in the silica geothermometer temperatures and reservoir chloride concentrations since the 1990s. This signifies that the shallow aquifer, in the immediate vicinity of the well feed zones, is stable and not showing any significant cooling or dilution. There is little change in the stable isotopes which support the stable chemistry.   Well 1016 in the south shows a substantial increase in HCO_3 compared to a nearby proxy well. However, without additional data it cannot be ascertained whether this is evidence for entry of less groundwater from shallow levels from the south.

An increase in the Na-K geothermometer temperatures by $10^{o}C$ to $16^{o}C$, may indicate an increase in the deeper source water temperatures, while the faster acting K-Mg geothermometer shows no major changes across the field. This again supports relatively stable temperatures in the shallower system but at a further distance from the aquifer feeding the wells.

Of the ten wells three had higher dilution in reservoir chloride and contained very high dissolved sulphide in the collected water samples; RR738 and RR865 (decreased ˜ 30 mg/L) located in the Western part of the field and RR887 (decreased ˜ 70 mg/L) at Government Gardens. The steam analyses from these wells showed CO_2/H_2S ratios less than 1 and high depletion of CH_4 relative to CO_2 and H_2S. The likely explanation is mixing of the shallow aquifer fluids with an enriched H_2S lower chloride fluid. This fluid may have formed by phase separation at depth and condensation and with accumulation of the relatively soluble H_2S at shallow depths. However why this fluid should appear now, what its range and extent is and whether it is a transient phenomenon, is uncertain. Modelling of gas reservoir processes may give some insight into its formation. H_2S gas concentrations exceeding CO_2 have not been observed in any other New Zealand geothermal field. The relative proportions of He with respect to Ar and N_2 have also shown interesting changes when compared to historical data. Relative He enrichment in the Western wells is, as high as or higher than at Ngapuna, Whakarewarewa and Kuirau, areas previously identified by Giggenbach and Glover (1992) as being main upflow zones. This suggests that the "upflow" zones identified may now cover a wider and more diffuse geographic area than identified previously. Whether this is due to increased flow of deeper, less boiled fluids to the surface and outward from the south and east as a consequence of the bore close programme or simply the result of lack suitable historical data is yet to be determined.

7.0   CONCLUSIONS

1. A geochemical survey of ten production wells over the Rotorua geothermal field was undertaken to collect a modern data set that could be used for comparison with historical data. The choice of suitable wells to sample was severely curtailed due to the implementation of the well closure programme.

2. The shallow aquifer feeding the wells over the last decade shows relatively minor changes in heat and reservoir chloride. This indicates stability and no deleterious processes are affecting the Rotorua geothermal system. Geothermometer temperatures of the deeper source waters appear to have increased typically by 16°C. Nevertheless three wells, two in Western Rotorua and one in Government Gardens show decreases in silica enthalpy and reservoir chloride.

3. These, three wells, which show more dilution than the others, appear to be mixing with a H$_2$S gas enriched fluid. The formation of this inferred fluid is a surprise and requires confirmation. Its genesis and effects on the local aquifer needs to be determined.

4. Helium enrichment relative to argon and nitrogen appears to have occurred in the Western part of the field. This suggests that the "upflow" zones may now cover a wider and more diffuse geographic or degassing is delayed because of increased pressures in the reservoir.

8.0   RECOMMENDATIONS

1. The apparent formation of a cooler H_2S gas rich phase which appears to be diluting the aquifer fluids is of concern as this could increase the "natural" gas flux to the surface and also cause problems if these mixed fluids are discharged in production wells. The limited and focused sampling in the study was not designed to follow up on this discovery. However work should be considered to determine the range and extent of the fluids and determine whether it is a transient phenomenon.

2. The study complements the Spring Study (Part 1) and both need to be combined to review the reservoir model of the field.

3. The study provides a baseline with which to compare future changes. As recommended in Part 1 for springs, the wells should also be sampled and reanalysed in 5 and again in 10 years time, thereafter to be reviewed.

9.0   ACKNOWLEDGEMENTS

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Table 1.   Location of sampled and proxy wells.

Well Number	Easting	Northing	Location	Cased (m)	Drilled (m)	Max T, °C	Enthalpy, kJ/kg	T (Enth), °C	T(Sil), °C	T(Sil), °C
									sampled	proxy
West Rotorua										
653	2794180	6333600	330 Old Taupo Rd	100	131	140	560	133	143	
825 (proxy for 653)	*2794297*	*6333681*	*64 Devon St*	*117.4*	*120.4*					*152*
738	2794720	6334070	46 Holland St	96.8	134	121			141	
816 (proxy for 738)	*2795063*	*6334088*	*19 Holland St*	*78*	*116.2*	*155*	*593*	*141*		*147*
741	2794880	6334920	Acacia Lodge Motel, 40 Victoria St	104.4	129.93	123			134	
627 (proxy for 741)	*2794954*	*6334861*	*7 Union St*	*94.5*	*124.9*					*135*
865	2795100	6334650	22 Malfroy Rd	98.5	105	130			141	
1016	2795350	6334060	288 Fenton St (adjacent to the Racecourse)	91	120	135			155	
638 (proxy for 1016)	*2795634*	*6334068*	*Rotorua Race Course, Fenton St*	*101.5*	*133*	*166*	*700*	*165*		*163*
Government Gardens										
885	2795560	6335790	Princes Gate Hotel	68	112.23	161	680	160	156	
680 (proxy for 885)	*2795645*	*6336028*	*QE Hospital*	*92*	*135.9*		*670*	*159*		*145*
887	2795720	6335330	Government Gardens	96.21	107.66	149			154	
Kuirau Park										
601A	2794570	6335500	131 Hinemoa St	137.7	173.7	153			142	
913	2794510	6335890	Aquatic Centre	121	146.5	152.5	865	203	166	
681 (proxy for 913)	*2794348*	*6335915*	*Kuirau Park*	*120*	*200*					*147*
619 (proxy for 913)	*2794267*	*6336405*	*96 Lake Rd (1 Tawera Rd)*	*56.5*	*195.1*					*114*
Ngapuna										
M25	2796178	6334563	Treatment Station	245	245	211			216	
889 (proxy for M25)	*2796178*	*6334580*	*Treatment Station*	*234.5*	*248*	*216*	*912*	*213*		*216*

Table 2.   Separated water chemical analyses of wells sampled in January and March 2003.

Laboratory Reference No		2300016	2300017	2300018	2300019	2300020	2300483	2300484	2300485	2300519	2300520
Collection Date		8/01/03	8/01/03	7/01/03	8/01/03	8/01/03	18/03/03	18/03/03	18/03/03	20/03/03	20/03/03
Well No.		RR653	RR887	RR865	RR913	RR738	RR885	1016	RR741	M25	RR601A
Bicarbonate (total)	mg/l	371	600	471	210	413	457	543	170	117	308
pH		8.42	7.88	8.35	9.06	7.96	8.63	7.77	7.44	7.58	8.44
Analysis temperature	°C	21	21	22	22	22	22	23	23	20	20
HCO_3/Date Analysed		9/1/03	9/1/03	9/1/03	9/1/03	9/1/03	19/3/03	19/3/03	19/3/03	21/3/03	21/3/03
Boron	mg/l	2.3	5.2	4.1	5.7	3.2	5.4	4.7	3.0	9.9	3.7
Calcium	mg/l	10.4	9.9	3.3	0.83	14.9	0.89	17.0	12.4	16.7	4.9
Chloride	mg/l	267	386	383	304	345	439	581	310	1516	242
Lithium	mg/l	1.5	3.6	2.6	3.0	1.8	2.5	2.5	1.9	2.6	1.6
Magnesium	mg/l	0.07	0.14	0.05	0.011	0.15	0.015	0.09	0.12	0.02	0.04
Potassium	mg/l	25	58	41	31	37	31	54	31	125	27
Silica (as SiO_2)	mg/l	253	277	243	325	245	290	293	218	343	249
Sodium	mg/l	328	504	473	289	413	514	577	389	950	302
Sulphate	mg/l	86	49	64	23	92	83	118	222	29	87
Sulphide (total as H_2S)	mg/l	43	190	141	14.2	111	110	154	41	95	44
H_2S/Date Analysed		9/1/03	9/1/03	9/1/03	9/1/03	9/1/03	19/3/03	19/3/03	19/3/03	21/3/03	21/3/03
Deuterium	$^o/_{oo}$	-36.3	-35.8	-36.2	-37.7	-36.2	-35.3	-34.8	-36.8	-36.2	-38.3
Oxygen 18	$^o/_{oo}$	-5.3	-4.9	-5.0	-5.5	-5.1	-4.6	-4.7	-5.2	-3.1	-5.7
Separation Pressure	bg	0.4	4	0.93	4.25	0.6	2.55	1.85	0.65	11.5	0.55

Table 3. Separated steam chemical analyses of wells sampled in January and March 2003.

Laboratory Reference No		2300012	2300013	2300014	2300015
Collection Date		8/01/03	7/01/03	8/01/03	8/01/03
Well No.		RR887	RR 865	RR 913	RR738
Carbon Dioxide	mmol/100 mol	1291	1746	829	8056
Hydrogen sulphide	mmol/100 mol	2587	3910	200	10921
Ammonia	mmol/100 mol	0.44	0.46	0.42	
Argon	mmol/100 mol	0.03	0.11	0.31	2.2
Helium	mmol/100 mol	<0.001	0.006	0.011	0.07
Hydrogen	mmol/100 mol	4.2	18.3	1.5	93
Methane	mmol/100 mol	0.34	2.2	22	26
Nitrogen	mmol/100 mol	1.5	5.5	30	143
Oxygen	mmol/100 mol	<0.001	<0.001	<0.001	<0.001
Separation Pressure	bg	4	0.93	4.25	0.6

Table 3 continued.

Laboratory Reference No		2300481	2300482	2300517	2300518
Collection Date		18/03/03	18/03/03	20/03/03	20/03/03
Well No.		RR885	1016	M25	RR601A
Carbon Dioxide	mmol/100 mol	781	1711	405	1027
Hydrogen sulphide	mmol/100 mol	115	371	167	93
Ammonia	mmol/100 mol	0.43	0.40	0.41	0.34
Argon	mmol/100 mol	0.03	0.11	0.06	0.58
Helium	mmol/100 mol	0.007	0.01	0.003	0.010
Hydrogen	mmol/100 mol	12.7	22	7.4	5.4
Methane	mmol/100 mol	2.2	3.9	0.51	10.2
Nitrogen	mmol/100 mol	3.8	7.8	5.1	31
Oxygen	mmol/100 mol	<0.001	<0.001	<0.001	<0.001
Separation Pressure	bg	2.55	1.85	11.5	0.55

Table 4.   Well discharge water compositions for sampled and proxy wells.

Well No	Sample No	Date	WHP, g	Enthalpy, kJ/gm	SP, bg	CT ºC	mg/L														
							TA	pH	Li	Na	K	Ca	Mg	Rb	Cs	Cl	SO4	B	SiO2	HCO3	H2Sd
RR601A	5503	21/07/83	0.3					9.05	1.4	309	26	4.5	0.03	0.24	0.2	267	62	3.1	235	291	
RR601A	6724/8/A	25/09/89	0.175			98.2	20	9	1.4	313	25	5.1	0.06	0.21	0.2	240	43	2.4	246	277	50
RR601A	6786/27/A	22/05/90	0.25			98.1	17	8.7	1.4	315	25	6	0.05	0.2	0.12	240	42	2.9	234	297	59
RR601A	2300520	20/03/03			0.55		20	8.44	1.6	302	27	4.9	0.04			242	87	3.7	249	308	44
RR653	6724/29/A	04/10/89	0.7			98.7	16	9.2	1.5	353	26	9.4	0.07	0.21	0.25	277	84	2.4	283	308	37
RR653	6786/24/A	22/05/90	0.7			99.1	19	9.2	1.4	349	40	9.4	0.06	0.19	0.18	262	77	2.7	277	306	38
RR653	2300016	08/01/03			0.4		21	8.42	1.5	328	25	10.4	0.07			267	86	2.3	253	371	43
RR738	6724/21/A	02/10/89	0.8			98.7	17	9.2	1.8	467	36	14	0.13	0.31	0.32	385	100	3.2	280	512	72
RR738	6786/9/A	14/05/90	0.75			98.4	20	9	1.8	452	34	13	0.12	0.29	0.27	393	219	3.4	263	287	68
RR738	2300020	08/01/03			0.6		22	7.96	1.8	413	37	14.9	0.15			345	92	3.2	245	413	111
RR627	5740/A	08/05/84				99	19	9.2	1.95	439	28	9.5	0.06	0.25	0.27	338	311	3.5	230	361	87
RR741	2300485	18/03/03			0.65		23	7.44	1.9	389	31	12.4	0.12			310	222	3.0	218	170	41
RR865	5762/A	04/05/84	1.6			99		9.35	2.52	542	41.5	2	0.09	0.33	0.34	460	146	5.1	297	332	102
RR865	5986/A	11/02/85	1.7			100	NA	NA	2.6	504	38.9	2.3	0.04	0.3	0.3	437	55	<5	265	NA	NA
RR865	6724/31/A	05/10/89	1.7			97.6	20	9.5	2.5	519	40	2.6	0.06	0.32	0.34	437	58	4.4	267	401	114
RR865	6786/28/A	22/05/90	1.6			98.8	18	9.2	2.6	518	39	2.8	0.06	0.3	0.26	426	56	4.9	269	342	132
RR865	2300018	07/01/03			0.93		22	8.35	2.6	473	41	3.3	0.05			383	64	4.1	243	471	141
RR885	5822/1/A	13/06/84				96.3	22	9.31	3.09	561	31.5	1.6	0.01	0.28	0.45	536	10	7	303	393	NA
RR885	5822/1/B	13/06/84	2.75	627	2.1			8.86	2.79	504	29	1.4	0.02	0.25	0.38	474	<1	6.4	275	465	111
RR885	5822/2/A	13/06/84				93.8	22	8.94	3.12	560	32	1.4	0.01	0.28	0.46	522	1	6.9	308	357	NA
RR885	5822/2/B	13/06/84	2.25	627	0.75			9.15	2.89	519	29	1.6	0.02	0.26	0.38	480	<1	6.3	271	472	93
RR885	6724/24/A	02/10/89	2.9			99.8	18	9.5	3	584	33	1.4	0.03	0.27	0.45	503	96	6.4	338	372	61
RR885	6786/21/A	21/05/90	3			98.8	17	9.4	2.9	555	31	1.5	0.02	0.25	0.36	444	30	6.5	321	348	81

Table 4.　Continued.

Well No	Sample No	Date	WHP, bg	Enthalpy, kJ/gm	SP, bg	CT, °C	mg/L														
							TA	pH	Li	Na	K	Ca	Mg	Rb	Cs	Cl	SO4	B	SiO2	HCO3	H2Sd
RR885	2300483	18/03/03			2.55		22	8.63	2.5	514	31	0.89	0.015			439	83	5.4	290	457	110
RR887	5767/A	07/05/84	4			99		9.58	2.89	622	54.5	1.4	0.03	0.39	0.41	529	316	7.3	337	398	104
RR887	6004/A	22/02/85	2.8			99	24	9.38	2.87	558	52	2	0.12	0.4	0.4	506	81	6.8	337	482	115
RR887	6004/B	22/02/85	2.8		2.8		24	8.65	2.6	518	47	2	0.08	0.4	0.4	457	151	6.2	320	511	144
RR887	6724/11/A	25/09/89	3.65			99.3	23	9.5	3	576	56	1.4	0.05	0.4	0.43	514	54	6	325	292	119
RR887	6724/11/B	25/09/89	3.65		3.65		20	8.6	2.6	528	50	1.4	0.08	0.36	0.39	461	46	5.3	293	461	164
RR887	2300017	08/01/03			4		21	7.88		504	58	9.9	0.14			386	49	5.2	277	600	190
RR889	5442/2	02/06/83	10.7	913	10.7		19	7.2	2.8	905	112	15.7	0.03	0.87	0.5	1403	8	9.8	331	99	4.7
RR889	5768/A	08/05/84	6			99		9.32	3.26	1138	123	17.6	0.05	0.99	0.57	1684	79	12.3	368	93	21
RR889	6724/13/A	27/09/89	11			100	19	9.6	3.6	1190	145	19	0.03	1.18	0.74	1865	11	12.7	448	50	21
RR889	6724/13/B	27/09/89	11		6.25		19	8.6	3	986	119	17	0.03	0.95	0.61	1542	7	10.5	368	62	81
RR889	6800/1/D	13/06/90	4.05				18	5.8	2.78	844	106	24.4	0.19	0.84	0.34	1379	210	9.8	320	138	85
M25	2300519	20/03/03			11.5		20	7.58	2.6	950	125	16.7	0.02			1516	29	9.9	343	117	95
RR681	5744/A	07/05/84	2			99	22	9.24	3.62	384	34.5	0.8	0.03	0.33	0.38	310	46	6.1	275	310	7
RR913	6171/A	15/10/85	4.9													332					
RR913	6305/A	27/05/86	6			99	19	9.5	4.21	369		<1	0.02	0.33	0.39	332	30		395	276	6
RR913	6305/B	27/05/86	6		2.6		19	9.4	3.83	335		<1	0.022	0.3	0.34	307	28		383	275	8
RR913	6306/B	27/05/86	5.6		3.5		19	9.3	3.79	338		1.6	0.035	0.18	0.15	301	37		334	273	10
RR913	2300019	08/01/03			4.25		22	9.06		289	31	0.83	0.011			304	23	5.7	325	210	14.2
RR638	6724/12/A	26/09/89	3.2			99.7	23	9.5	2	570	55	18	0.1	0.39	0.37	593	75	4	350	350	86
RR638	6786/31/A	23/05/90	3.4			99	18	9.5	1.9	525	51	18	0.09	0.36	0.26	479	68	4.3	348	271	112
RR638	6786/31/B	23/05/90	3.4		3.4		18	7.8	1.7	475	46	16	0.08	0.33	0.23	431	63	4.1	316	399	158
1016	2300484	18/03/03			1.85		23	7.77	2.5	577	54	17.0	0.09			581	118	4.7	293	543	154

Table 5.   Well discharge steam compositions for sampled and proxy wells.

Well No	Sample No	Date	WHP, bg	Enthalpy, kJ/kg	SP, bg	mmol/100 mol								
						CO2	H2S	H2	He	N2	Ar	NH3	CH4	O2
RR601A	2300518	20/03/03			0.55	1027	93	5.4	0.01	31	0.58	0.34	10.2	0.001
RR738	2300015	08/01/03			0.60	8056	10921	93	0.07	143	2.2	0	26	0.001
RR865	2300013	07/01/03			0.93	1746	3910	18.3	0.006	5.5	0.11	0.46	2.2	0.001
RR885	5822/1/S	13/06/84	2.75	627	2.1	770	91	9.2		2.1		0.52	1.4	
RR885	5822/2/S	13/06/84	2.25	627	0.75	481	67	4.4		1.9		0.45	0.62	
RR885	2300481	18/03/03			2.55	781	115	12.7	0.007	3.8	0.03	0.43	2.2	0.001
RR887	6004/S	22/02/85	2.8		2.8	1738	300	2.6		0.65		0.81	0.097	
RR887	6724/11/S	25/09/89	3.65		3.7	1095	207	3.05	0.0034	2.01	0.0271		0.269	0.006
RR887	6786/18/S	21/05/90	1.9		1.9	18354	4810	70	0.047	346			5.1	4.7
RR887	6786/18/SA	21/05/90	0.4		0.4	2150	460	9	0.006	77			0.62	
RR887	2300012	08/01/03			4.0	1291	2587	4.2	0.001	1.5	0.03	0.44	0.34	0.001
RR889	5442/2	02/06/83	10.7	913	10.7	1168	377	13.3		11.7			0.93	
RR889	6724/13/S	27/09/89	11		6.25	200	70	3.9		146	1.68		0.191	12.2
M25	2300517	20/03/03			11.5	405	167	7.4	0.003	5.1	0.06	0.41	0.51	0.001
RR913	6305/S	27/05/86	6		2.6	235	6.4					0.28		
RR913	2300014	08/01/03			4.9	829	200	1.5	0.011	30	0.31	0.42	22	0.001
RR638	6724/12/S	26/09/89	3.2		3.2	560	359	9.4	0.0101	23.2	0.275		1.43	
RR638	6786/312/s	23/05/90	3.5		3.4	2670	570	40	0.028	80	0.98		5.9	
1016	2300482	18/03/03			1.85	1711	371	22	0.01	7.8	0.11	0.4	3.9	0.001

Table 6. Well discharge steam compositions for sampled and proxy wells, concentration per mole dry gas. Xg is the gas fraction in steam.

Well No	Sample No	Date	WHP, bg	Enthalpy, kJ/kg	SP, bg	Xg mmol /mol	mmol/ mol								
							CO2	H2S	H2	He	N2	Ar	NH3	CH4	O2
2300518	RR601A	20/03/03			0.55	11.7	880	80	4.6	0.0086	27	0.50	0.29	8.7	<0.0009
2300015	RR738	08/01/03			0.60	192.4	419	568	4.8	0.0036	7.4	0.11		1.4	<0.0001
2300013	RR865	07/01/03			0.93	56.8	307	688	3.2	0.0011	0.97	0.02	0.08	0.39	<0.0002
5822/1/S	RR885	13/06/84	2.75	627	2.1	8.7	881	104	10.5		2.4		0.59	1.6	
5822/2/S	RR885	13/06/84	2.25	627	0.75	5.6	866	121	7.9		3.4		0.81	1.1	
2300481	RR885	18/03/03			2.55	9.2	853	126	13.9	0.0076	4.2	0.03	0.47	2.4	<0.0011
	RR887	*				280	785	58	76.4	0.0033	75	0.71	0.02	4.7	
6004/S	RR887	22/02/85	2.8		2.8	20.4	851	147	1.3		0.32		0.40	0.05	
6724/11/S	RR887	25/09/89	3.65		3.7	13.1	838	158	2.3	0.0026	1.5	0.02		0.21	0.005
6786/18/S	RR887	21/05/90	1.9		1.9	236	778	204	3.0	0.0020	15			0.22	0.199
6786/18/SA	RR887	21/05/90	0.4		0.4	27.0	797	171	3.3	0.0022	29			0.23	
2300012	RR887	08/01/03			4.0	38.8	332	666	1.1	<0.0003	0.39	0.01	0.11	0.09	<0.0003
	RR889	*				2.2	630	268	11.9	0.0062	88	1.1	0.85	0.78	
5442/2	RR889	02/06/83	10.7	913	10.7	15.7	744	240	8.5		7.4			0.59	
6724/13/S	RR889	27/09/89	11		6.25	4.3	461	161	9.0		232	2.63		0.44	0.0**
2300517	M25	20/03/03			11.5	5.9	692	285	12.6	0.0051	8.7	0.10	0.70	0.87	<0.0017
6305/S	RR913	27/05/86	6		2.6										
2300014	RR913	08/01/03			4.9	10.8	765	185	1.4	0.0102	28	0.29	0.39	20	<0.0009
	RR638	*				0.9	607	201	2.9	0.0065	184	2.7	0.42	1.1	
6724/12/S	RR638	26/09/89	3.2		3.2	9.5	587	377	9.9	0.0106	24	0.29		1.5	
6786/312/s	RR638	23/05/90	3.5		3.4	33.7	793	169	11.9	0.0083	24	0.29		1.8	
2300482	1016	18/03/03			1.85	21.2	809	175	10.4	0.0047	3.7	0.05	0.19	1.8	<0.0005

* From Giggenbach and Glover (1992). Sampled between 1989-90.

* * Air Corrected

Table 7. Well discharge water compositions for proxy wells only.

Well No	Sample No	Date	WHP, bg	Enthalpy, kJ/gm	SP, bg	CT ºC	mg/L														
							TA	pH	Li	Na	K	Ca	Mg	Rb	Cs	Cl	SO4	B	SiO2	HCO3	H2Sd
RR619	5515	21/07/83				81.5		7.15	0.9	175	12	10.2	0.06	0.13	0.23	160	30	3.1	155	212	
RR619	6724/9/A	25/09/89				76.2	21	7.8	1	189	15	10	0.07	0.13	0.25	156	34	3.1	162	225	<1
RR619	6786/3/A	14/05/90				64	19	7.71	1.1	185	14	10	0.2	0.12	0.2	159	33	3.3	157	228	<1
RR638	5740/1/A	04/05/84	3.25					9.6	2.25	681	55	9.6	0.06	0.42	0.39	704	103	5.9	332	251	66
RR638	6724/12/A	26/09/89	3.2			99.7	23	9.5	2	570	55	18	0.1	0.39	0.37	593	75	4	350	350	86
RR638	6786/31/A	23/05/90	3.4			99	18	9.5	1.9	525	51	18	0.09	0.36	0.26	479	68	4.3	348	271	112
RR638	6786/31/B	23/05/90	3.4		3.4		18	7.8	1.7	475	46	16	0.08	0.33	0.23	431	63	4.1	316	399	158
RR680	6724/17/A	28/09/89	3.6			100.5	22	9.5	3.1	572	40	1.5	0.04	0.3	0.46	540	25	6.9	314	361	48
RR680	6724/17/B	28/09/89	3.6		3.6		22	8.4	2.7	498	34	1.6	0.04	0.26	0.39	469	29	5.9	280	338	106
RR680	6786/15/A	18/05/90	0.6			98.8	17	8.8	2.6	483	31	8.5	0.33	0.23	0.33	499	20	6	266	379	68
RR680	6786/15/B	18/05/90	1.45		1.45		16	8	2.4	473	31	7.5	0.31	0.24	0.3	499	18	5.8	255	344	91
RR681	5744/A	07/05/84	2			99	22	9.24	3.62	384	34.5	0.8	0.03	0.33	0.38	310	46	6.1	275	310	7
RR816	5509/1	21/07/83	1.45					9.35	2.2	513	46	4.8	0.14	0.34	0.31	432	87	4.1	275	405	
RR825	5752/A	07/05/84	0.85			99	22	9.26	1.66	391	27.5	2.2	0.03	0.24	0.28	274	135	2.7	296	281	36

Table 8.   Geothermometer temperatures and reservoir Chloride (Cl_{res}).

Well No	Sample No	Date	Tsil, ºC *	H, kJ/gm	Cl_{res}, mg/L	Na-K (Arnórsson), ºC	Na-K (Giggenbach), ºC	K-Mg, ºC
rr601A	5503	21/07/83	137	575	248	187	219	184
RR601A	6724/8/A	25/09/89	140	587	222	183	215	169
RR601A	6786/27/A	22/05/90	136	574	223	182	215	172
RR601A	2300520	20/03/03	142	597	228	192	224	180
RR653	6724/29/A	04/10/89	149	627	251	176	209	167
RR653	6786/24/A	22/05/90	147	621	238	214	243	187
RR653	2300016	08/01/03	143	600	250	179	212	166
RR738	6724/21/A	02/10/89	148	624	350	180	212	168
RR738	6786/9/A	14/05/90	144	606	360	178	211	167
RR738	2300020	08/01/03	141	593	327	192	224	166
RR627	5740/A	08/05/84	135	569	315	166	199	173
RR741	2300485	18/03/03	134	562	298	183	215	164
RR865	5762/A	04/05/84	152	641	415	179	212	181
RR865	5986/A	11/02/85	144	608	400	180	212	195
RR865	6724/31/A	05/10/89	145	610	400	180	212	187
RR865	6786/28/A	22/05/90	145	612	389	178	211	186
RR865	2300018	07/01/03	141	594	367	189	221	192
RR885	5822/1/A	13/06/84	153	646	482	157	190	217
RR885	5822/1/B	13/06/84	151	638	458	158	192	197
RR885	5822/2/A	13/06/84	154	651	468	158	191	217
RR885	5822/2/B	13/06/84	148	623	450	156	190	197
RR885	6724/24/A	02/10/89	161	679	445	157	191	194
RR885	6786/21/A	21/05/90	157	664	396	156	190	200
RR885	2300483	18/03/03	156	657	425	162	195	207
RR887	5767/A	07/05/84	161	678	468	190	222	217
RR887	6004/A	22/02/85	161	678	448	195	227	184
RR887	6004/B	22/02/85	163	688	438	193	225	188
RR887	6724/11/A	25/09/89	158	667	457	199	230	206
RR887	6724/11/B	25/09/89	158	666	453	197	228	191
RR887	2300017	08/01/03	154	651	384	214	244	185
RR889	5442/2	02/06/83	214	914	1318	221	250	253
RR889	5768/A	08/05/84	208	890	1332	209	239	245
RR889	6724/13/A	27/09/89	221	950	1425	220	249	268
RR889	6724/13/B	27/09/89	218	933	1370	219	248	257
RR889	6800/1/D	13/06/90	216		1379	223	251	
M25	2300519	20/03/03	216	927	1424	227	255	271
RR681	5744/A	07/05/84	147	619	282	192	224	196
RR913	6305/A	27/05/86	172	727	286			
RR913	6305/B	27/05/86	175	743	285			
RR913	6306/B	27/05/86	167	705	289			
RR913	2300019	08/01/03	166	700	296	208	238	214
RR638	6724/12/A	26/09/89	163	690	522	198	229	190
RR638	6786/31/A	23/05/90	163	688	422	199	230	189
RR638	6786/31/B	23/05/90	163	687	417	199	230	187
RR1016	2300484	18/03/03	155	655	554	196	227	192

* Cristobalite for all wells except for wells RR889 and M25 where quartz is the controlling polymorph

Table 9. HCO$_3$-Cl-B used to construct Figure 8. All 2003 data reduced to atmospheric pressure.

Well No	Sample No	Date	Cl, mg/L	B, mg/L	HCO$_3$,mg/L	HCO3%	Cl%	50B%
5503	rr601A	21/07/83	267	3.1	291	40.8	37.4	21.7
6724/8/A	RR601A	25/09/89	240	2.4	277	43.5	37.7	18.8
6786/27/A	RR601A	22/05/90	240	2.9	297	43.5	35.2	21.3
2300520	RR601A	20/03/03	248.3	3.8	300.9	40.7	33.6	25.7
6724/29/A	RR653	04/10/89	277	2.4	308	43.7	39.3	17.0
6786/24/A	RR653	22/05/90	262	2.7	306	43.5	37.3	19.2
2300016	RR653	08/01/03	267	2.3	371	49.3	35.5	15.3
6724/21/A	RR738	02/10/89	385	3.2	512	48.4	36.4	15.1
6786/9/A	RR738	14/05/90	393	3.4	287	33.8	46.2	20.0
2300020	RR738	08/01/03	354	3.28	173.2	25.1	51.2	23.7
5740/A	RR627	08/05/84	338	3.5	361	41.3	38.7	20.0
2300485	RR741	18/03/03	310	3	170	27.0	49.2	23.8
5762/A	RR865	04/05/84	460	5.1	332	31.7	43.9	24.4
6724/31/A	RR865	05/10/89	437	4.4	401	37.9	41.3	20.8
6786/28/A	RR865	22/05/90	426	4.9	342	33.8	42.1	24.2
2300018	RR865	07/01/03	397	4.26	167.8	21.6	51.0	27.4
5822/1/A	RR885	13/06/84	536	7	393	30.7	41.9	27.4
5822/2/A	RR885	13/06/84	522	6.9	357	29.2	42.6	28.2
6724/24/A	RR885	02/10/89	503	6.4	372	31.1	42.1	26.8
6786/21/A	RR885	21/05/90	444	6.5	348	31.2	39.7	29.1
2300483	RR885	18/03/03	475.1	5.84	406.2	34.6	40.5	24.9
5767/A	RR887	07/05/84	529	7.3	398	30.8	40.9	28.3
6004/A	RR887	22/02/85	506	6.8	482	36.3	38.1	25.6
6724/11/A	RR887	25/09/89	514	6	292	26.4	46.5	27.1
2300017	RR887	08/01/03	428	5.8	327.2	31.3	41.0	27.7
5768/A	RR889	08/05/84	1684	12.3	93	3.9	70.4	25.7
6724/13/A	RR889	27/09/89	1865	12.7	50	2.0	73.1	24.9
6800/1/D	RR889	13/06/90	1379	9.8	138	6.9	68.7	24.4
2300519	M25	20/03/03	1837	12	81.45	3.2	72.9	23.8
5744/A	RR681	07/05/84	310	6.1	310	33.5	33.5	33.0
6305/A	RR913	27/05/86	332		276	45.4	54.6	0.0
2300019	RR913	08/01/03	339	6.35	155.3	19.1	41.8	39.1
6724/12/A	RR638	26/09/89	593	4	350	30.6	51.9	17.5
6786/31/A	RR638	23/05/90	479	4.3	271	28.1	49.6	22.3
2300484	RR1016	18/03/03	618	5.01	501.9	36.6	45.1	18.3

Table 10. Isotopic measurements for geothermal bores sampled in 2003 and historical data.

Well No	Date	T(Sil), °C	‰		mg/L		
			$d^{18}O$	d^2H	Cl	HCO$_3$	SO$_4$
601A	Jul-83	135	-5.92	-39.0	250	291	62
601A	Sep-89	140	-5.88	-39.3	222	297	43
601A	Jan-03	142	-5.98	-39.7	228	315	89
825*	May-84	150	-5.68	-38.4	248	281	135
653	Jan-03	143	-5.6	-37.8	250	378	88
816*	Jul-83	150	-5.25	-37.7	391	405	87
738	Jan-03	141	-5.35	-37.4	327	424	94
627*	May-84	134	-5.56	-37.4	317	--	311
741	Jan-03	134	-5.37	-37.8	299	175	228
865	May-84	151	-5.19	-39.1	416	332	146
865	Feb-85	143	-5.30	-38.9	402	--	55
865	Jan-03	141	-5.19	-37.1	367	488	66
680*	Sep-89	157	-4.97	-38.7	461	494	20
885	Jan-03	156	-4.73	-35.8	423	493	90
887	May-84	159	-4.87	-36.7	471	398	31
887	Sep-89	158	-5.35	-39.2	454	292	54
887	Jan-03	154	-4.92	-35.9	384	664	54
619*	Jul-83	111	-5.89	-38.6	157	212	30
619*	Sep-89	110	-6.25	-39.0	146	225	34
681*	May-84	145	-5.01	-35.4	284	310	46
913	Jan-03	166	-5.6	-38.1	296	233	26
638*	May-84	158	-4.88	-36.7	627	251	103
638*	Sep-89	161	-5.03	-38.7	523	350	75
1016	Jan-03	155	-4.89	-35.6	554	156	125
M9*	Aug-83	213	-3.53	-37.8	1378	--	--
M9*	May-84	205	-3.45	-37.4	1344	93	78
M9*	Sep-89	218	-3.46	-36.2	1372	62	11
M25	Jan-03	216	-3.27	-36.6	1427	141	35

*Proxy well