GEOCHEMISTRY OF ORAKEIKORAKO GEOTHERMAL FIELD

G.L. Lyon* and
D.S. Sheppard**

*Institute of Nuclear Sciences
**Chemistry Division, DSIR, Lower Hutt

ABSTRACT

Recent geochemical sampling has confirmed that spring discharge water is near neutral with chloride contents less than 375 ppm. Maximum temperatures estimated from alkali geothermometry and mixing models are 220-230°C. Water isotopic data show no evidence of lake water intrusion and only a small oxygen shift due to high temperature interaction with rocks. The chemical compositions indicate that the highest chloride water rises in the south, and bicarbonate waters from the north mix in the central part of the field.

INTRODUCTION

The Orakeikorako geothermal area is situated on the Waikato River about 35 km south-west of Rotorua. In January 1961, the field was partially flooded by Lake Ohakuri, a hydro-electric reservoir on the Waikato River. Extensive areas of modern sinter with hot pools and a small geyser are all that remain of the original spectacular collection of pools, geysers and sinter (Lloyd, 1972).

The sampling programme was designed to determine if changes were apparent due to flooding of part of the field, and to try and model the field using modern chemical methods of analysis of gas and water samples. This is part of a regional study including the fields of Te Kopia, Waikite, Ngatimariki, Waiotapu, Waimangu and Reporoa,

WATER AND STEAM COMPOSITIONS

Water and steam samples were collected from hot pools, fumaroles, steam vents and surface waters in June 1980. Figure 1 shows the sampling localities. We attempted to identify sample localities as listed by Lloyd (1972), but changes to the field have occurred since his surveys, and it proved difficult to locate and identify a few features. Some features may be new. Analyses and collection procedures were similar to those used in other surveys (e.g., Sheppard & Robinson, 1980).

The compositions of a representative selection of the water samples collected are listed in Table 1. It is evident that the Orakeikorako field emits geothermal waters at boiling temperatures and considerably more dilute than other large fields in the vicinity, e.g., Broadlands, Waiotapu, Wairakei, where the natural spring waters can contain over 1000 ppm chloride, compared with the 375 ppm maximum at Orakeikorako. Other smaller fields along the Paeroa Fault have lower chloride contents.

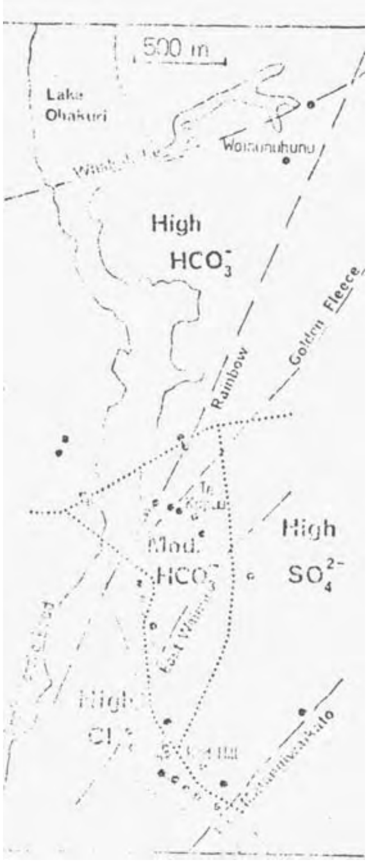

Fig. 1. Orakeikorako geothermal area. Large dots are sample sites. Dashes are major faults.

Geothermal waters can be broadly classified by the relative proportions of the three anions SO_4^{2-}, Cl^-, and HCO_3^- as shown in Fig. 2. Chloride is the major anion of deep geothermal fluids, where it is concentrated by either leaching from country rock, emanation from the heat source or from a deep brine or from any combination of these. Deep waters contain very limited sulphate (<20 ppm in general). High sulphate containing waters are present in most geothermal fields with a high or

Table 1: Compositions of some Orakeikorako waters

Site no.	T°C	pH	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{++}	Ca^{++}	Al	Fe	SiO_2	B	NH_3	F^-	Cl^-	$SO_4^=$	HCO_3^-(T)
WAIHUNUHUNU																		
970	52	7.4	0.5	113	3	.02	<.01	.47	3.4	.07	<.05	112	<2	.11	2.2	41	20	189
674	80	7.1	0.9	171	6	.04	<.01	.31	3.9	.06	<.05	148	<2	<.10	2.8	71	27	251
TE KATUA																		
95	95	8.6	3.8	334	43	.45	.56	<.02	1.8	.11	<.05	354	1	.10	10.1	314	79	153
98	83	7.4	3.6	300	44	.45	.55	.13	2.0	.09	<.05	333	<2	.10	9.8	304	111	188
120	98	8.5	3.0	324	49	.48	.56	<.02	1.6	.20	<.05	392	3	<.10	10.1	322	100	224
710	43	2.5	2.8	197	47	.51	.42	.80	2.8	.57	8.4	299	<2	.66	6.0	190	444	
146	98	8.7	3.2	263	34	.35	.48	.0?	1.6	.19	.08	282	2	<.10	6.6	228	83	243
882	94	2.0	<0.1	1	1	<.01	<.01	.10	.26	12.6	.30	97	<2	4.0	.72	3	1493	
210	81	9.9	2.3	302	31	.35	.56	<.02	1.2	.28	<.05	253	7	.14	11.0	314	99	85
WEST BANK																		
589	53	6.9	2.4	216	21	.20	.50	.11	4.6	.07	<.05	222	<2	.10	1.8	180	47	263
25	84	7.5	2.8	324	17	.19	.59	<.02	.68	.32	<.05	274	7	.17	7.8	299	72	279
526	86	7.6	3.4	334	in	.17	.49	<.02	1.1	.17	<.05	263	6	.19	13.0	349	84	159
RED HILL SPRINGS																		
369	99	9.8	3.3	326	35	.40	.63	.02	1.2	.27	<.05	337	6	1.4	11.5	346	63	100
421	100	8.8	2.8	263	29	.32	.55	.55	2.4	.16	<.05	246	4	.15	9.4	275	57	167
451	100	7.3	2.0	239	22	.22	.43	.34	3.0	.26	<.05	220	<2	,26	8.7	262	93	56
957	96	2.4	<0.1	7	3	.01	<.01		3.6	13.6	3.82	132	<2	6.2	.5	3	350	
487	98	9.5	2.6	303	34	.37	.55	<.02	.76	.17	<.05	271	8	.19	9.0	317	60	135

perched water table due to interaction of H_2S with oxygenated groundwaters, and these are quite superficial. Bicarbonate results from the reaction of CO_2, H_2O and aluminosilicates in 'condensation zones', where CO_2-containing steam condenses into groundwaters to produce the aggressive acid solutions. Condensation zones commonly overlie and surround geothermal fields.

The waters of Orakeikorako occupy an arc in Fig. 2 from the sulphate corner to high relative chloride - 60 to 70% and back to the bicarbonate corner. The waters with the highest relative sulphate (e.g. springs 882, 957) are from acid, high temperature boiling pools into which steam and H_2S are being condensed producing low-chloride high-sulphate waters. The bulk of the water samples fall about a line linking high bicarbonate with chloride dominant waters, with some almost stagnant waters containing appreciable sulphate. The highest bicarbonate waters are those from Waihunuhunu in the north. These springs have very high flows and moderately high temperatures, and it is of interest that they fall near Waikite/Puakohurea, Parengarenga, and Golden Springs waters in Fig. 2. The Rainbow fault (Fig. 1) is an extension of the Paeroa fault, on which the Te Kopia, Waikite and Puakohurea springs lie. Perhaps these waters flow along the fault emerging at these points, or that all these waters originate in the same way, related by the fault structure. The major faults crossing the field are shown on Fig. 1. Between these faults are several normal faults with comparatively small surface displacements. Hot springs now emerge along the faults - especially the Golden Fleece and Rainbow Faults. Fig. 1 also shows the chemistry compiled from the ratios of Fig. 2 and delineates the different types of fluid with their relation to the known faults, and each other.

The high bicarbonate waters occur at Waihunuhunu and in small springs on the west bank. There does not appear to be any structural relationship between the two areas, and while chemistry is

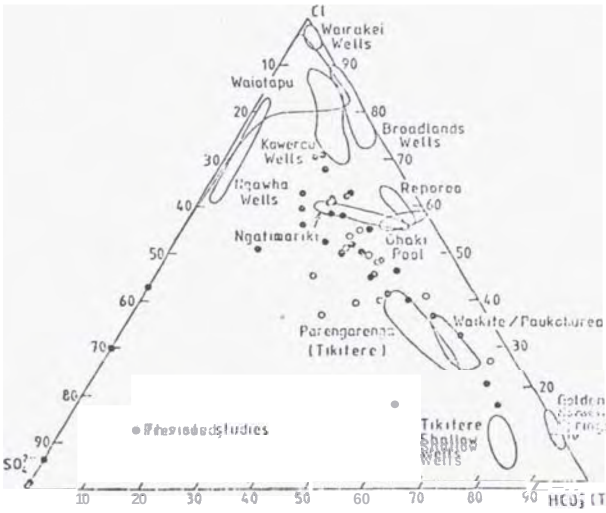

Fig. 2. SO_4-Cl-HCO_3 relationships showing Orakeikorako analyses.

similar in that HCO_3^- exceeds Cl^-, their different character **implies** different origins. **High-**sulphate waters exist on the periphery of the field where steam heating is common.

The more chloride rich waters form a tongue from south to north, primarily between the **Matangi**waikato and East Wainui faults. The Artist's Palette springs (those along and above the Rainbow and Golden Fleece Faults) are intermediate in composition between the high chloride and the high bicarbonate waters.

For each water sample, silica and cation **geothermo**meters have been applied but the indicated temperatures do not show any regular pattern. For a better understanding, the mixing model technique of Truesdell and Fournier (1976) was applied and Fig. 3 shows a plot of chloride against enthalpy calculated from the quartz equilibration temperatures.

It is clear that of three possible processes (steam loss, steam gain by steam heating, and dilution), the dominant process causing the variation in composition is dilution by a hot low chloride water. Some steam loss (and gain) and some dilution by cold local water may play a minor part. The deepest source water composition determined by this procedure ("A" on Fig. 3) is about 280 ppm chloride and about 230°C (1000 J/g), about the highest values determined by the NaKCa geothermometer. The low chloride end members of the dilution trend in Fig. 3 are the Waihunuhunu spring waters. Several acid sulphate (surface oxidised) waters are only coincidentally of similar Cl and SiO_2 compositions.

The generalised relationship between $\delta^{18}O$ and δD in the analysed water samples is shown in Fig. 4. Three steam samples are highly depleted (not shown in Fig. 4), and all the more enriched samples are from acid pools. The mean cold water composition is (-6.95, -42.4) where the values in brackets are respectively $\delta^{18}O_{SMOW}$ and δD_{SMOW} (in ‰). This is **significantly** different from the mean Waikato River water composition (-5.37, -34.8).

From Fig. 4 **it** can be seen that the mean meteoric water composition is close to the line $\delta D = 8.\delta^{18}O + 13$ which represents most North Island meteoric waters. Almost all hot spring waters can be fitted inside a cone of enrichment limited by lines from the freshwater composition with slopes of 2 and 5 (Giggenbach, 1978). This **isotope** enrichment is due to loss of vapour from the water, by boiling or evaporation. Most of the hot springs form a group near to A, with a mean composition of about (-5.2, -37) and chloride content about 300 ppm, and are near 100°C. As their mineral content shows they are not merely fresh waters, they originate from deep geothermal fluids, and in many cases boiling is obvious.

As **it** is not possible to measure the relative proportions of steam and water in a hot spring, the original isotopic composition prior to boiling must be estimated by assuming an original temperature. Assuming that equilibrium vapour separation has occurred near to 220°C an original composition (B, Fig. 4) of about (-6.4, -44) and 230 ppm chloride is calculated. As the springs have scattered values, this estimate is not a precise one. Figure 4 shows that variations from the composition A, are easily explained by dilution with cold water with zero chloride, or a dilute water of low chloride and light isotope composition such as the Waihunuhunu springs. This trend can also be seen in plots of the isotope composition against Cl. The inferred deep water composition B has a deuterium isotope composition indistinguishable from the cold waters, but with only about 0.5‰ oxygen-18 enrichment. A further significant group of hot springs (C in Fig. 4) with a mean composition of (-4.3, -34) is mostly cooler than boiling, several of these springs are about 85 C. They can easily be derived by evaporation from group A composition, at temperatures of 80-100°C.

The chloride-isotope plots also show that the spring waters with high **bicarbonate/chloride** ratio are not close to the main group composition. Also, two pools which are both high sulphate, high chloride waters, are either mixtures of normal spring water and acid sulphate waters, or pools of stagnant chloride water where H_2S can be oxidised in the pool. They are isotopically enriched due to evaporation or steam heating, but not to the high degree shown by the low chloride, acid sulphate waters.

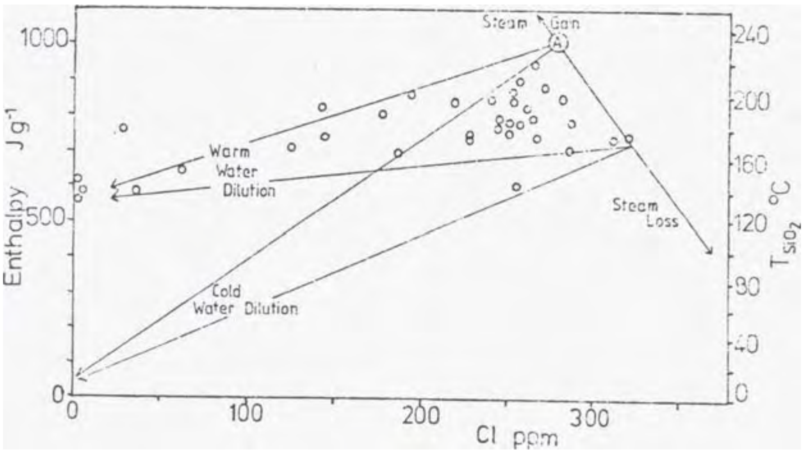

Fig. 3. Enthalpy relative to chloride
A is the inferred deep water.

Eight samples of water were collected for $^{34}S/^{32}S$ and $^{18}O/^{16}O$ analyses of the sulphate ions. Oxygen-18 isotopic fractionation, if assumed to be in equilibrium with a deep water of $\delta^{18}O = -6.3‰$, indicatg temperatures between 180° and 300° with 220–240 being the most reliable estimate.

GAS COMPOSITIONS

One of the first impressions a geothermalist receives on visiting Orakeikorako is the lack of H_2S in the air. Even on still days, the characteristic smell is absent. There are two reasons for this evident from the analyses in Table 2: (1) the low gas contents in the south of the field where C/S ratios are low; (2) the higher C/S ratios in the north of the field where gas contents are higher.

N_2/Ar ratios are generally between 50 and 100, an indication that this ratio is determined by the inclusion of atmospheric gases in the samples; the oxygen content supports this conclusion. Such contamination is unlikely to be due to direct ingress of air due to poor sampling (except in samples from 370 and 421); rather it is caused by the presence of the gases from heated groundwater.

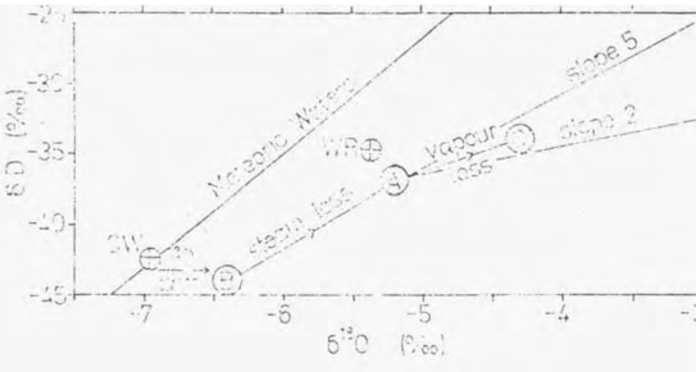

Fig. 4. Generalised stable isotope diagram for Orakeikorako (see text) - WR = Waikato River, CW = cold waters.

Methane and hydrogen contents are very low in comparison with most New Zealand fields. Orakeikorako gas compositions are similar to the gases from Wairakei and Te Kopia.

The empirical geothermometer derived by D'Amore and Panichi (1980) was used but indicated temperatures are scattered, though generally increasing southward. Stable isotope analyses of the gases indicate $\Delta^{13}C\ (CH_4\text{-}CO_2)$ temperatures about 320°, about 30°C cooler than at Wairakei.

The $\delta^{13}C_{PDB}$ (CO_2) values are mostly in the range -2 to -3‰. This is considerably heavier than most other New Zealand geothermal gases, which are about -7‰ except for Wairakei -3 to -5‰ and some White Island analyses near -3‰. Since sedimentary carbon usually has $\delta^{13}C$ values of 0 ± 2%, it appears that Orakeikorako has a higher proportion of crustal CO_2 and less magmatic CO_2 than do the other New Zealand geothermal areas.

CONCLUSIONS

The thermal waters of Orakeikorako are dilute compared with waters of other geothermal fields. Three water types are recognised -

a) superficial sulphate waters derived from the steam heating of surface pools;
b) waters with a higher chloride/bicarbonate ratio, i.e. $Cl:HCO_3$ >3:1. These occur in the south of the field;
c) waters with $Cl:HCO_3$ <3:1. These appear to result from a mixing of bicarbonate waters, typified by the Waihunuhunu springs, with the waters of the south of the field.

The isotopic composition of the water supports the chemical interpretation of a mixing of a water of about 280 ppm Cl^- (assuming a reservoir temperature of 230°C) with water of Waihunuhunu composition.

The gases of Orakeikorako also show a differentiation between those in the north and those in the south, with those in the north being similar to a gas collected at Waikite, some 30 km away along the Paeroa fault. The gases in the southern part of the field are very similar to Wairakei gas compositions and suggest that the field is open to circulation of meteorically-derived ground waters.

It is evident that we believe that the Orakeikorako geothermal system derives from two sources of hot water - one in the north and one in the south. The chemical differentiation of the waters and gases within the field suggests that waters arising along the northern faults differs from the southern faults (particularly the Matangiwaikato). As the Waihunuhunu springs lie on a branch of the Paeroa fault (Lloyd, 1972) the similarity between the Waikite/Puakohurea waters and gases and that from the Waihunuhunu springs suggests a common, or at least analagous, origin.

The waters at Orakeikorako are quite dilute in comparison to most geothermal fluids.

There is no evidence that the hydrology or chemistry of the Orakeikorako have changed due to the damming of the Waikato River.

ACKNOWLEDGEMENTS

The authors wish to thank the N.Z. Geological Survey, Rotorua, for the loan of their boat, and to thank Brian Robinson for the sulphate isotope analyses. Mark James and Derek Stannard assisted with isotopic analyses. We also thank the proprietor of Orakeikorako Geyserland for his hospitality and assistance.

REFERENCES

D'Amore, F., Panichi, C., 1980, Evaluation of deep temperatures of hydrothermal systems by a new gas geothermometer. Geochimica et Cosmochimica Acta. 44, 549-556.

Giggenbach, W.F., 1978, The isotopic composition of waters from the El Tatio geothermal field, Northern Chile. Geochimica et Cosmochimica Acta. 42, 979-988.

Lloyd, E.F., 1972, Geology and Hot Springs of Orakeikorako. N.Z. Geological Survey Bulletin 85.

Sheppard, D.S., Robinson, B.W., 1980, A chemical and isotopic survey of the Waiotapu, Reporoa and Waikite hydrothermal discharges. Geothermal Circular DSS-4.

Truesdell, A.H., Fournier, R.O., 1976, Calculation of deep temperatures in geothermal systems from the chemistry of boiling spring waters of mixed origin. Second UN Symposium on the Development and Use of Geothermal Resources, San Francisco, Proceedings 1, 837-844.

Table 2: Gas compositions (mmole/mole, water free)

Site no.	T°C	CO_2	H_2S	NH_3	He	H_2	Ar	O_2	N_2	CH_4
140	86	972	6.37	0.0025	0.0022	0.038	0.27	4.4	15.9	0.63
120	100	803	7.76	<0.0092	0.064	2.87	4.89	0.023	176.0	5.20
136	99	829	4.95	0.057	0.049	0.688	1.76	29.5	134.0	1.39
882	94	959	9.16	0.062	0.015	3.0	0.46	0.0062	26.9	1.81
593	78	988	7.08	0.0033	0.0143	0.0086	0.112	0.036	4.54	0.154
1001	82	920	1.47	0.0038	0.0198	2.73	1.34	0.62	65.4	1.?7
368	96	938	2.93	0.057	0.0031	1.0	0.836	5.33	51.2	0.653
370	96	154	15.4	<0.061	0.030	0.067	7.71	173.0	649.0	0,043
451	100	877	43.6	0.108	0.013	0.520	1.29	0.096	77.7	0.182
963	100	848	93.1	0.434	0.116	6.78	1.11	0.293	49.1	1.32
421	100	95.9	30.5	<0.034	0.017	0.261	8.41	155.0	680.0	0.10