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THE CHEMISTRY OF THE BROADLANDS GEOTHERMAL AREA NEW ZEALAND

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ABSTRACT. Broadlands is a hydrothermal area in the Taupo Volcanic Zone of the North Island of New Zealand. The surface activity is limited in extent, and the natural heat flow from the area, 17,500 kcals/sec, is small compared with other areas in the zone. Scientific investigations and later drilling, however, have shown that the area of the deep hot water system (9km²) is comparable to that at Wairakei. Hot water at temperatures up to about 300°C but usually tapped by drillholes

Hot water at temperatures up to about 300° C but usually tapped by drillholes at 260° to 270°C contains in approximate quantities, NaCl (1625 ppm), KCl (265 ppm), boron (32 ppm), and silica as major constituents and occurs at depths down to approximately 2420 meters. Dissolved gas in the water is mainly carbon dioxide, at a concentration level near 0.14 molal. Concentrations of heavy metals in the water are low, but precipitates and sinters derived from the water contain high concentrations of arsenic, antimony, and heavy metals. D/H values in the water are similar to those present in local streams to the east, indicating that a high proportion of the hot water is derived from a meteoric source.

Trends in the chemistry of drillhole fluids with time provide a clearer picture of the physical conditions existing in the underground system, before and during exploitation. Slight deposition of calcite occurs in the casing of a drillhole, as originally predicted from the early chemistry of the water discharges.

INTRODUCTION

Following successful geothermal power developments at Wairakei large-scale drilling was carried out at Broadlands to determine the extent and characteristics of the deep high temperature water. This was preceded by a Wenner resistivity survey across the area which delineated a zone of low resistivity, to depths of approximately 550 m, of size comparable to the Wairakei geothermal field. The results from subsequent geochemical, geophysical, and geological investigations were used to locate sites for exploratory drillholes. To date nineteen holes ranging in depth from 762 to 2420 m have been drilled in an area of some 9 km². This paper discusses the chemistry of the fluids discharged from the hot springs and drillholes and correlates the results with the geology and physical conditions at depth in the field.

The locality of Broadlands with respect to other geothermal areas in the Taupo Volcanic Zone is shown as an inset in figure 1. The field extends some 3.6 km along both sides of the Waikato River in the Taupo-Reporoa Basin, some 27 km northeast of Taupo. The natural activity is limited to a few hot springs and hot water seepage into the Waikato River and minor areas of mudpools and steaming ground. The natural heat flow was estimated by Dickinson (ms) as 17,500 kcal/sec which can be compared with 101,000 kcal/sec for the Wairakei area (Dawson and Dickinson, 1970).

The major surface activity in the northern part of the field was Ohaki Pool (fig. 1) a hot spring that covered an area of 850 m² and discharged 10 1/sec of hot water at 98°C before the area was drilled. In addition there was a smaller spring close by and scattered zones of

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hot water seepage into the of the Ohaki Pool (see w hot springs occurred 3 km of mud pools and dark km southwest of Ohaki Pe two latter areas was below less than 70°C.



Fig. 1. Locality of the springs position of Broadlands within the Tau

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hot water seepage into the Waikato River 1.2 km to the east and south of the Ohaki Pool (see water compositions, table 1). A smaller area of hot springs occurred 3 km south-southwest of Ohaki Pool, and a number of mud pools and dark colored thermal pools lay approximately 1.0 km southwest of Ohaki Pool. The flow from individual springs in the two latter areas was below 1 l/sec, and temperatures were in all cases less than 70°C.





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During the early chemical survey work in the area, the extent of not water scepage and runoff from Broadlands was measured. Water amples were collected from cold streams within the area and from the Waikato River upstream and downstream of the visible surface activity to check on high chloride water flows. The survey showed that little more than 30 to 35 1/sec of hot chloride water appeared at the surface.

Studies of the surface and subsurface geology at Broadlands and the mineralogy and hydrothermal alteration of rock cores taken during brilling were made by Grindley and Browne (ms) and Browne and Ellis 1970). A generalized stratigraphic sequence of the rocks, taken from Grindley and Browne (ms), is shown opposite.

Holes drilled in the eastern side of the field, at the deepest level, penetrated basement argillite and graywacke, as did the deepest hole in the field, hole 15 in the west. Most of the other holes drilled in the west terminated in ignimbrite. The porosity of the formations was in the range 10 to 40 percent, but where there was extensive hydrothermal alteration, it was considerably reduced.

Table 4 shows data for the 19 holes drilled and discharged at Broadlands. Most of the holes were drilled to depths between approximately 750 and 1400 m except hole 15 which was drilled to 2418 m. Downhole temperatures were high and in the range 260° to 300°C, while pressures at deeper levels in the holes, before discharge, approximated to hot hydrostatic pressure and were higher than the vapor pressure of the water at any particular depth.

The highest temperature in most holes was near the hole bottom, but those having high mass outputs reached near maximum temperature within 20° to 30° between 427 and 610 m. Poor production holes had a more gradual or erratic temperature increase throughout their length, while holes 4 and 13 had a temperature inversion at deeper levels.

The discharge enthalpies of many holes, after continuous discharge, were higher than the supply water at maximum measured temperatures. These holes were supplied by a steam/water mixture rather than a single hot water phase. Significant pressure falls occurred in the drillholes after continuous discharge, and pressures measured in some drillholes indicated the presence of a fluid less dense than water at the respective temperatures (vapor/water mixture). Many holes after drilling and standing closed for a few days built up high gas pressures at the wellhead as a result of accumulation of gas in the holes and consequent depression of the water levels.

The permeability of the rocks penetrated by many drillholes at Broadlands is apparently too low to allow steady state production. Drawdown of hot water levels in holes during production allows hydrostatic pressures to fall to the vapor pressures at the producing horizons. Boiling and the formation of steam within the system are induced and propagated by the lowering of pressures and the consequent transfer of heat from rock to water. The chemistry of the Broadlands geothermal area New Zealand 51

Stratigraphic sequence of rocks at Broadlands

		Thickne	ss
Formation	Content	Feet	Meters
Taupo Pumice Haparangi Pumice Wairakei Breccia (Lapilli Tuff)	Pumice alluvium and ash showers. Pumiceous sands, rhyolitic gravel, and sand. Pisolitic, pumice-rhyolite lapilli tuff, and breccia.	100-300	30-91
Huka Falls Formation	Alternating thick beds of lacustrine siltstone, locally diatomaceous, with pumiceous sandstone, grit, and tuff.	100-1000	30-305
Ohaki Rhyolite	Crystal rich, biotite-hornblende quartz-plagioclase rhyolite. Commonly pumiceous and spherulitic, locally breceiated.	0-1400	0-427
Upper Waior a Formation	Tuff-breccia with pumice and rhyolite lapilli; siltstone underlain by sedi- mentary pumice tuffs.	600-900	183-274
Broadlands Rhyolite	Dense, flowbanded, plagioclase, thyo- lite, locally perlitic or glassy. Upper (2) and lower (1) flow units.	0-1500(2)	457
Rautawiri Breccia	Coarse, crystal-vitric-lithic breccias with fragments of pumice rhyolite, ignimbrite, siltstone, and argillite.	500-900	152-274
Rangataik i Ignimbrite	Crystal-rich, quartz-plagioclase ignim- brite, locally lenticulitic, passing up into unwelded crystal-vitric tuff.	100-1400	30-427
Upper Waikora Formation	Thin-bedded, non-volcanic sandstone, siltstone, grit. Conglomerate beds with argillite and minor pumice pebbles.	0-200	0-61
Lower Waiora Formation	Pale gray, coarse crystal-vitric tuff with quartz (possibly unwelded upper part of ignimbrite sheet).	0-350	0-107
Lower Waikora Formation	Thin-bedded, non-volcanic sandstone, siltstone, grit, conglomerate beds with argillite pebbles.	0-300	0-91
Wairake i Ignimbrit e	Crystal rich, quartz-plagioclase ignim- brite, locally lenticulitic, small gray- wacke inclusives.	150+	46÷
Graywacke basement	Dense, indurated, massive graywacke and dark fractured, vein argillite with poor bedding.		

CHEMISTRY OF THE NATURAL ACTIVITY AT BROADLANDS

Table 1 lists the chemical compositions of waters discharged from springs at Broadlands. As the number of near boiling springs in the area was small, the extent to which surface chemistry could be used for predicting underground water compositions and temperatures was limited. However, the presence of a major feature such as Ohaki Pool,

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TABLE 1									
Analysis of a representative group	o of springs at Broadlands								

S P T	Date of	Flow		_	Concentration in water (ppm)											
i	1965	l/sec 🛛	ſ°C	$\mathbf{p}\mathbf{H}$							÷					
n				÷												
g No.					Li	Na	ĸ	Rb	Cs	Ca	Mg	F	Cl	Br	I	SO4
1	16.6	10	98	7.0	7.4	860	82	0.1	1.2	8.5	0.215	5.2	1040	3.0	0.6	100
3 4 5 6	16.6 16.6 16.6 17.6	Nil 0.3 0.3 0.3	25 75 57 19	2.6 8.0 8.7 2.8	4.6 3.6 2.6 3.35	440 430 374 410	43.5 31.5 28 22			$33 \\ 28 \\ 16.2 \\ 5.7$		2.2	681 525 362 539	 1.5	0.3 	530 132 52 347
7 A* B*	17.6 16.6 16.6	Nil 0.5 0.3	42 61 66	7.3 7.9 7.9	3.95 3.6 3.3	$500 \\ 415 \\ 410$	21 30.5 31			$7.0 \\ 46 \\ 15.3$		4.2 2.4 2.4	$638 \\ 492 \\ 443$	1.7	0.3	185 162 82

Spring 1 is Ohaki Pool

Analysis of spring 2 (Fig. 1) is identical to analysis of spring 1.

* A and B are samples collected from seepage into the Waikato River

(table 1) with a high temperature and large flow, enabled certain predictions to be made.

The hot waters discharged from springs in the Broadlands area were mainly of the neutral pH, chloride-bicarbonate type. Chloride concentrations ranged from approximately 300 to 1000 ppm, and the similar constituent ratios, such as Cl/B, Cl/F, and Na/Li, in springs suggested a common reservoir of hot water beneath the area with varying degrees of dilution and evaporative concentration by boiling. Acid pools, with little or no overflow, had similar constituent ratios to the near neutral pH springs.

Cl/B ratios in the waters ranged from 8 to 11 which were low compared with values found in rhyolitic areas such as Wairakei, Waiotapu, Orakei-Korako, and Rotorua. Low to very low ratios were found also at Kawerau (Mahon, 1962b), Tokaanu (Mahon and Klyen, 1968), and Ngawha (Ellis and Mahon, 1966), where the rocks are either andesitic or sedimentary. The Na/Li ratios and rather high ammonia concentrations at Broadlands were similar to those for the Kawerau waters.

High sulphate and ammonia concentrations in the lower pH spring waters and the presence of sulphur on sinter and in areas of steaming ground suggested that some steam heating of surface waters occurred. Concentrations of minor elements such as rubidium, caesium, fluoride, bromide, iodine, calcium, and magnesium were of the same order as found in hot waters at Wairakei, and ratios of these elements to either chloride or sodium were also similar to those at Wairakei. Cl/Br and Cl/As ratios at Broadlands for example were approximately 800 and 820 respectively compared with ratios of 850 and 1000 at Wairakei.

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TABLE 1 (continued)

_Con	icentra	tion	in wat	er (ppr	n)	Molecular ratio								
				CO,			of chloride to				0	f sodiı	ım to	
B	SiO2	As	NII_3	as HCO ₃	H ₂ S	в	F	As	Br	SO₄	Cs	Li	к	Ca
32.1	338	1.5	3.8	680	1.0	9.9	107	560	780	28.1	3250	35	17.8	176
		to 3.9						to 1465						
18.9	280		5.8	Nil	1.0	11.0				3.5		29	17.2	23.2
14.8	280		0.1	322	1.0	10.8	128			10.8		36	23.2	26.8
11.0	207		1.9	430	1.0	10.8	88			18.8		43	22.7	40.2
20.6	250	1.2	1.6	CO2 38	1.0	8.0		950	810	4.2		37	31.7	125
23.7	232	1.4	1.1	188	1.0	8.2	81	962	846	9.3		38	40.5	124
13.6	214		2.8	307	1.0	11.0	110		•	8.2		35	23.1	15.7
13.1	225	·	2.3	385	1.0	10.3	99	·		14.6		38	22.5	16.6

Silica concentrations of between 280 and 340 ppm in the spring waters would correspond to an underground water temperature of between 190° to 200°C. This assumes that the deep waters were just saturated with respect to quartz and were not affected by dilution or loss of SiO₂ on route to the surface, and decrease in temperature resulted from boiling with no loss of heat by conduction. (Mahon, 1966; Fournier and Rowe, 1966). The Na/K ratios of between 17 and 23 corresponded to underground equilibration temperatures of about 200°C between rock minerals and water (Ellis and Mahon, 1967).

- The low concentrations of constituents such as calcium, magnesium, and fluoride, which at high temperature are controlled at a low level by mineral equilibria, indicated high temperatures at deeper levels and substantiated the impressions obtained from the silica concentrations and Na/K ratios.

Estimates of the carbon dioxide concentration in the deep water from surface chemistry, using the methods of Ellis (1970), gave values ranging from 1.6×10^{-3} to 3.25×10^{-1} molal. The low concentration was obtained for a deep water temperature of 200°C, while the high value corresponded to a deep temperature of 250°C. (At Wairakei, Waiotapu, and Orakeikorako experience showed that estimates of minimal underground temperatures from SiO₂ concentrations and Na/K ratios were approximately 50° to 60°C lower than those found on drilling.) The higher value was of the same order as carbon dioxide concentrations found in steam discharged from two areas of steaming ground (0.6 molal).

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TABLE 2 Analyses of water in drillholes at Broadlands

				·		Cor	icentra	ation i	in water	r (ppn	Concentration in water (ppm)									
Hole	Date	рН 20°С	Li	Na	K	Rb	Cs	Ca	Mg	F	Cl	Br	I							
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 17	$\begin{array}{c} 1. \ 2.66\\ 23. \ 8.66\\ 28. \ 4.67\\ 6. \ 9.67\\ 14.11.67\\ 14.12.67\\ 14. \ 5.68\\ 29. \ 2.68\\ 14. \ 5.68\\ 29. \ 2.68\\ 13.12.68\\ 10.10.68\\ 6. \ 2.69\\ 3. \ 4.70\\ 16. \ 1.70\\ 24. \ 4.70\\ 24. \ 4.70\\ 2. \ 4.70\\ 2. \ 4.70\\ \end{array}$	$\begin{array}{c} 8.3\\ 8.3\\ 8.0\\ 8.35\\ 9.1\\ 7.4\\ 8.55\\ 7.9\\ 8.45\\ 8.6\\ 8.25\\ 8.25\\ 8.25\\ 8.25\\ 8.25\\ 8.15\\ 7.83\\ 8.25\\ \end{array}$	$\begin{array}{c} 10.9\\ 11.7\\ 12.2\\ 11.8\\ 4.9\\ 1.2\\ 15.0\\ 11.4\\ 12.7\\ 9.5\\ 12.2\\ 10.0\\ 12.6\\ 10.5\\ 11.5\\ 6.25\\ 10.0\\ 11.2\\ 11.8\\ \end{array}$	1065 1050 1045 1075 1400 435 1300 975 930 975 930 910 1020 1510 980 880 1066 570 1010 1110 950	$\begin{array}{c} 152\\ 224\\ 213\\ 218\\ 39\\ 234\\ 232\\ 203\\ 142.5\\ 218.5\\ 198\\ 200\\ 175\\ 200\\ 175\\ 207\\ 85\\ 224\\ 237\\ 206.5 \end{array}$	$\begin{array}{c} 0.6\\ 2.2\\ 1.8\\ 2.0\\ \hline \\ 2.4\\ 2.9\\ 2.4\\ 1.1\\ 1.7\\ 0.95\\ 2.2\\ 0.9\\ 1.8\\ 0.51\\ 1.86\\ 1.84\\ 1.6\\ \end{array}$	$\begin{array}{c} 0.6\\ 1.7\\ 1.8\\ 1.4\\ - 2\\ 1.8\\ 1.6\\ 1.5\\ 1.4\\ 1.25\\ 1.3\\ 1.5\\ 1.55\\ 0.47\\ 1.88\\ 1.80\\ 1.7\\ \end{array}$	$\begin{array}{c} 4.6\\ 2.2\\ 3.0\\ 3.0\\ \hline \\ 3.0\\ \hline \\ 2.0\\ 1.1\\ 7.3\\ 2.8\\ 2.0\\ 1.1\\ 7.3\\ 2.8\\ 2.0\\ 5.7\\ 8.55\\ 4.82\\ 9.0\\ 2.5\\ \end{array}$	0.08 0.02 0.013 0.1 0.36 0.05 0.02 0.13 0.015 0.7 0.13 7.46 0.007 0.18 0.05	$\begin{array}{c} 6.7 \\ 7.3 \\ 6.1 \\ 4.5 \\ - \\ - \\ 8.4 \\ 8.0 \\ 6.2 \\ 6.4 \\ 3.2 \\ 4.5 \\ 3.2 \\ 6.8 \\ 6.05 \\ 8.6 \\ 3.9 \\ 7.4 \end{array}$	1701 1743 1801 1851 1142 28 1823 1823 1823 1709 1244 1794 1546 1668 1482 1750 528 1778 1985 1720	$\begin{array}{c} \hline 6.4 \\ 6.6 \\ 6.7 \\ \hline 5.2 \\ 6.3 \\ 5.9 \\ 3.6 \\ 7.0 \\ 5.1 \\ 5.25 \\ 4.2 \\ 5.8 \\ 1.6 \\ 4.5 \\ 4.6 \\ 4.6 \\ \end{array}$	$\begin{array}{c} 1.4\\ 0.8\\ -\\ 0.95\\ 0.35\\ 0.6\\ 0.4\\ 0.1\\ 0.1\\ 0.1\\ 0.7\\ 0.4\\ 0.30\\ 0.25\\ 0.35\\ 0.6\\ 0.5\\ 0.5\\ 0.5\\ 0.5\\ 0.5\\ 0.5\\ 0.5\\ 0.5$	$\begin{array}{c} 43\\ 8\\ 6\\ 29\\ \hline \\ 15\\ 6\\ 3.5\\ 4.0\\ 11.5\\ 10\\ 25\\ 6.5\\ 6.0\\ 7.1\\ 45\\ 5.5\\ 4.0\\ 7.1\\ 6.5\\ 5.5\\ 4.0\\ 7.1\\ 6.5\\ 5.5\\ 4.0\\ 7.1\\ 6.5\\ 5.5\\ 4.0\\ 7.1\\ 6.5\\ 5.5\\ 4.0\\ 7.1\\ 7.1\\ 7.1\\ 7.1\\ 7.1\\ 7.1\\ 7.1\\ 7.1$						
27 44 awerau	1965 1965 u	8.5 8.6	13.2 14.2	1200 1320	200 225	3.0 2.8	2.7 2.5	$17.5 \\ 17.5$	0.05 0.035	8.1 8.3	2156 2260	5.9 6.0	0.6 0.3	25 36						
8 16	1969 1969	9.0 8.0	5.5 5.6	740 720	$\begin{array}{c}130\\131\end{array}$	0.9 0.55	0.5 0.48	$1.1 \\ 3.2$	0.39 0.31	5.2 3.0	$1262 \\ 1233$	6.2 5.4	0.2 0:2	10.5 14.0						

CHEMISTRY OF THE FLUIDS DISCHARGED FROM DRILLHOLES AT BROADLANDS

Chemical results .-- The analyses of the water and steam discharged from drillholes during initial discharge are shown in tables 2 and 3. Concentrations in the water are given in parts per million parts of water, for waters separated from the discharge at boiling point and atmospheric pressure. Chloride concentrations are given for atmospheric pressure separation and for the original deep water. Gas concentations are given as either millimoles per 100 moles steam condensate or as a weight percentage. For comparison, the analyses of waters discharged from deep drillholes in the Wairakei and Kawerau Geothermal Fields are listed.

General comments on results .- The waters discharged from the Broadlands drillholes were lower in mineral content than the deep Wairakei waters but similar to that of the deep waters at Kawerau and Waiotapu. Atmospheric pressure chloride concentrations ranged from approximately 1200 to 2000 ppm, except for hole 6 which discharged water at a temperature well below boiling point, containing approximately 30 ppm chloride.

At depth the waters were saturated with silica in equilibrium with quartz at the water temperatures and near to saturation with calcite.

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TABLE 2 (continued)

Conc	rentrat	ion	n wate	er (ppm) Cl in					Mole	ular rat	io		-		
			* Total	** Total	water		of chloride to						of sodium to			
В	SiO ₂	As	NHa	HCO ₃		B	F	As	Br	SO4	Cs	Ĺi	ĸ	Rb	Ca	
48.1	565		12.0	230	1233	10.8	136			109	10625	30	11.0	6505	105	
48.4	805	5.7	2.1	178	1177	11.0	128	650	615	590	3840	97	8.0	1775	909	
55.3	725	4.0	4.0	174	1245	9.9	160	951	615	800	3750	26	0.0	0155	0.00	
56.5	880	5.7	2.3	282	1150	10.0	220	685	622	170	4955		0.J 8.4	100*	605	
23.4			1.5	1410	1000	14.8					1000	86	16.2	1995	025	
1.2	180	-	1.1	2284	25	6.9				5.1		110	10.5			
82.7	1000		1.0	910	1002	6.7			790	825	3705	0.11	15.0	2010	2.9	
52.6	796	5.7	2.3	157	1220	11.0	114	690	665	1440	4350	20.2	71	1950	1020	
43.95	805	4.5		134	1147	11.9	114	800	650	1155	4970	20	7.1	1440	505	
54.8	635	4.1	1.2	553	891	6.9	107	640	780	295	3330	28.0	10.05	2075	510	
48.9	805	5.5	1.35	78	1213	11.2	150	690	575	485	4800		70.00	0000	1440	
43.7	400	1.0	2.4	1820	1196	10.8	258	3265	680	165	4635	45.5	120	2230	245	
48.0	750	3.2	1.9	162	1144	10.6	199	1100	715	605	4910	40.0	15.0	3905	940	
47.4	844	5.7	1.45	218	961	9.6	248	550	795	670	2700	40.0	8.3	1005	710	
37.5	1126		2.0	310	1150	14.2	138	000	680	665	4920	49.9	8.9	3035	765	
40.6	265		12.0	555	441	4.0	47		7.1.4	89	4230	21.0	8.7	2190	325	
46.0	765		1.9	115	1215	11.8	111		\$00	875	95.44	20.2	11.4	4105	115	
58.5	635		3.05°	250	1367	10.3	973		600	1245	4195	20.2 20.0	7.0	2000	360	
48.2	875		1.9	175.5	1150	10.9	194		844	995	9775	29.9	8.0	2240	215	
									011	~~U	5115	25.0	1.8	2205	660	
28.4	660	4.7	0.15	23	1528	232	145	970	820	925	9000	074	10.0	1400	100	
28.9	650		0.15	19	1600	23.8	145	570	850	170	2000	21.4	10.2	1490	120	
			-	-			× 10		030	170	5585	48.0	10.0	1750	130	
61.2	815		0.5	24	860	6.3	130		460	325	0/55	41.0	0.7	905F	1150	
58.8	800		1.3	138	840	6.4	220		515	240	0695	20	9.7	3033 4965	1170	

* Total $NH_1 + NH_4$ expressed at NH_3 . ** Total HCO_3 means $CO_2 + HCO_3^- + CO_3^{2-}$ expressed as HCO_3 .

The waters were chemically similar to the spring waters. Lower bicarbonate contents in the deep waters resulted from the higher temperatures and smaller extent of rock/water interaction, and the low oxygen fugacity at depth accounted for the low sulfate concentrations.

The deep waters had a high total gas content, the carbon dioxide concentration of approximately 0.14 molal being ten times greater than found at Wairakei. The gas concentration was between that found in New Zealand hydrothermal areas in a mainly volcanic rock environment, for example, Wairakei and Orakeikorako (0.005-0.028 molal), and in a sedimentary rock environment, for example Ngawha (3.5 molal). The weight percentage of carbon dioxide plus hydrogen sulfide in steam separated from the discharges at 125 psig (PSI gauge) varied from about 2 to 12 percent.

Within the Broadlands Field the chemistry of the deep waters was similar. Some variation occurred in the concentration of constituents, but constituent ratios such as Na/Li, Cl/Br, Cl/As, Na/Rb, and Cl/Cs were similar, suggesting a common water supply.

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CO ₂ /H	$\begin{array}{c} 335\\ 3560\\ 355.8\\ 355.8\\ 355.8\\ 355.8\\ 355.9\\ 355.9\\ 355.5$
y wt of 1 stream 0 psig H ₂ S	$\begin{array}{c} 0.013\\ 0.067\\ 0.067\\ 0.058\\ 0.058\\ 0.058\\ 0.056\\ 0.056\\ 0.056\\ 0.025\\ 0.025\\ 0.026\\ 0.025\\ 0.025\\ 0.036\\ 0.025\\ 0.036\\ 0.025\\ 0.$
gas in CO _a	$\begin{bmatrix} 6.8 \\ 5.$
y wt of n total harge 11_S	0.013 0.027 0.027 0.035 0.035 0.035 0.035 0.035 0.035 0.035 0.035 0.035 0.035 0.009 0.010 0.010 0.010 0.011 0.010 0.011 0.011 0.011 0.011 0.011 0.011 0.011 0.011 0.011 0.011 0.011 0.011 0.011 0.011 0.011 0.011 0.011 0.012 0.000 0.012 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.00000 0.00000 0.00000 0.000000
disc disc disc disc disc disc disc disc	6.7 6.7 1.86 6.7 6.54 6.54 6.54 6.54 5.11 1.95 6.7 3.81 0.55 1.95 1.95 1.55 1.95 1.55 1.95 1.55 1.95 1.55 1.95 1.55 1.95 1.55 1.95 1.55 1.10 1.55 0.55 1.10 1.55 0.55 1.10 1.55 0.55 1.10 1.55 0.55 1.55 1
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uttotal total noles/ noles H ₂ S	11.5 11.5
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nalyzed noles/ noles H_S	25.7 25.7 25.5 25.5 25.5 25.5 25.5 21.5 25.5 21.5 25.5 21.5 21.5 25.5 21.5
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E BTU/Ib	1150 5530 5530 5530 5530 5530 5530 5530
S.P. psig	20 20 20 20 20 20 20 20 20 20
W.H.P. psig	45 445 198 167 167 167 175 175 175 110 110 110 110 108 173 250 252 253 100 110 108 175 175 108 175 108 175 175 175 175 175 175 175 175 175 175
Date	 28. 2.66 30.9.566 30.9.566 30.9.568 22.2.3.2.568 3.5.68 3.5.69 3.7.968 4.70 7.470 2.470 3.470
Hole no.	N 0 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1

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TABLE 4

		•	-		Maximum temperature after drilling and					
Hole	Drilled	depth	Solid ca	ased to	5	stabilization				
110.	Meters	Feet	Meters	Feet	°C	Meters	Fcet			
1	1397	4583	607	1992	278 .	1378	4550			
2	1034	3392	417	1368	287	1021	3350			
3	912	2992	469	1539	281	905	2969			
4	1019	3343	-517	1696	273	915	3002			
5	1351	4432	842	2762	244	1265	4150			
6	1083	3553	653	2142	143	960	3149			
7	1119	3671	538	1765	279	1067	3501			
8	776	2546	444	1457	273	771	2529			
9	1368	4488	500	1640	- 294	1341	4399			
10	1087	3566	497	1630	. 280	1082	3550			
11	760	2493	484	1588	271	756	2480			
12	1369	4491	656	2152	274	1341	4399			
13	1080	3543	806	2644	276	823	2700			
14	1282	4206	588	1929	297	1250	4101			
15	2418	7933	1547	5075	298	2165	7103			
16	1404	4606	623	2044	277	1387	4550			
17	1082	3550	576	1890	291	1036	3399			
18	1215	3986	538	1765	290	1195	3920			
19	1078	3537	527	1729	272	744	2441			

Deep chloride values for waters were calculated from chloride concentrations in waters flashed to atmospheric pressure, knowing the enthalpy of the discharge and the deep water temperature (SiO₂ concentrations). Deep chloride concentrations fell into two categories. Holes on the northwest side of the field (2, 3, 4, 8, 9, 11, 12, 13, 15, 17, 18, and 19) and hole 1 in the northeast produced from hot water containing 1150 to 1250 ppm chloride while holes on the southeast side of the field (7, 10, and 14) were supplied by hot water of 800 to 1000 ppm chloride.

The Cl/B ratios showed a trend across the field. Significant changes were apparent between holes 5 and 15 and the remainder of the northwestern holes and between holes in the west and southeast of the field. The low ratios of between 4 and 7 in the latter area probably resulted from the association with basement argillites and graywackes which generally have a higher boron content than the igneous rocks. The graywacke did not show a high grade of hydrothermal alteration, but the type and degree of alteration expected from contact of this rock with 270°C water has not been established.

The ratio of 9.6 in hole 14 (this hole did not penetrate into graywacke) was between the values found in the west and southeast, and the basement graywacke appears to be close enough to the hole to influence water compositions. The Cl/B ratios of between 14 and 15 in holes 5 and 15, which produced from ignimbrite, were the highest in the field. Hot waters associated with ignimbrite in other Taupo Volcanic Zone hydrothermal areas are known to have relatively high Cl/B ratios, and for example, waters from Orakeikorako drillholes had ratios varying from 25 to 35. Holes 9 and 17, which obtained most of their water supply

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from the Rautawiri Breccia (Browne and Ellis, 1970), had ratios of approximately 11.8 to 12, while holes drawing from a shallow level within the Ohaki Rhyolite and Upper Waiora Formation such as 3, 4, and 18 had ratios of between 9.9 and 10.3. Holes 2, 8, 11, 12, and 19 which could draw water from both the Ohaki Rhyolite and Rautawiri Breccia had intermediate ratios of around 11.

Constituent ratios such as Na/Li, Na/Rb, Cl/F, Cl/Cs, Cl/Br, and Cl/As were remarkably similar to those at Wairakei, illustrating the overall similarity of volcanic rock compositions in the two areas. The higher values of the ratios Cl/SO₄, Na/Ca, and the silica concentrations and the lower ratios of Na/K at Broadlands reflect the higher temperatures in this area. The high boron, ammonia, carbon dioxide, and bicarbonate concentrations at Broadlands are likely to result from the sediments interbedded with the volcanic rocks and the relatively shallow sedimentary basement in this area.

Base metal sulfides (Pb, Zn, Cu) were found in cores taken from holes 7, 10, 14, 15, and 16 (Browne and Ellis, 1970). Apart from 14, these holes penetrated the argillite-graywacke basement, the holes on the southeast at a depth of 914 to 1219 m and hole 15 at around 2286 m. Hole 14 was apparently also close to the basement.

Most of the sulfide mineralization in the southeast occurred close to or in the sediments, while in hole 15 it occurred at a depth considerably deeper than the majority of the other northwestern holes. The close association of the metal deposits with the basement sediments indicated that sulfide mineralization was influenced to some extent by these rocks.

Supply water temperatures.—The silica concentrations (Mahon, 1966) and the Na/K ratios (Ellis, 1967) in the drillhole waters were used to assess the temperature conditions in the deep aquifers.

Table 5 shows the maximum temperatures recorded in the drillholes by engineers of the New Zealand Ministry of Works, with a geothermograph or a resistance thermometer, and the temperatures calculated from Na/K ratios and silica concentrations. The latter results were obtained after the holes had been opened for a short period and water compositions had become constant. The maximum temperatures measured by physical methods were not necessarily recorded in permeable zones in the rock formations. The maximum temperatures in these zones ranged from 260° to 285°C.

The temperatures estimated from the Na/K ratios were in most cases closer to the measured maximum temperatures than were the silica temperatures.

It appeared that water of 270° to 280°C rose up through the country rock from below 1220 m and lost steam close to the production zones. Due to the rapidity of water movement and the slow readjustment of the Na/K ratio to an equilibrium value at a new temperature, the ratios in the discharges did not represent the temperature conditions at the production depth. The possibility the drillholes drew water up The chemistry of the Broadlands geothermal area New Zealand 59

TABLE 5

A comparison of temperatures estimated from silica concentrations and Na/K ratios in waters, with maximum temperatures measured down drillholes

	Physical	Temper	ature °C
Hole no.	measurement*	Na/K	SiO ₂
I	278	230	236
2	287	278-292	262
. 3	281	277-288	252
4	273	268-280	260
5	2.14	197-200	
6	143	192	
7	279	252-260	270-280**
8	273	300	255.5
9	294	292	259-261
10	280	240-242	244.5
11	271	290	261
12	274	220	212
13	276	282	255
14	297	277	259.5
15	298	273	290**
16	277	234	184
17	291	298	255.5
18	290	288	240.5
19	272	292	267

* Measurements made by Ministry of Works, Wairakei.

** Results suspect or unreliable.

Silica concentrations and temperatures have been corrected for enthalpy variations.

from deeper levels was also suggested by the low Cl/B ratio in holes 7 and 10.

The silica supply water temperatures of holes 2, 3, 4, 8, 9, 11, 13, 14, 17, and 19, of between 252° and 267°C were remarkably similar. Supply water temperatures in the eastern field were generally lower than those in the northwest, for example, holes 1, 10, and 16 were supplied by water of temperature less than approximately 245°C, while holes 7 and 14 had supply water temperatures between 250° and 260°C. Comparison of these temperatures, with measured temperatures and corresponding pressures in the field, indicated that the Ohaki Rhyolite, Broadlands Rhyolite, and Rautawiri Breccias in the west of the field and the Broadlands Rhyolite in the east were major aquifers. The rhyolites at Broadlands appear to play an important role both in the storage of fluids and in determining the migration paths.

Gases.—Table 3 shows the concentrations of carbon dioxide and hydrogen sulfide in the Broadlands drillholes. During the initial discharge period of the drillholes the carbon dioxide and hydrogen sulfide concentrations in total discharge ranged from 108 to 2770 and 2.8 to 20.8 millimoles/100 moles water respectively. These concentrations may be compared with those of 20 and 0.6 millimoles/100 moles water of carbon dioxide and hydrogen sulfide originally present in the deep Wairakei waters. The ratio of CO_2/H_2S in the different discharges

TABLE 6 Analysis of gases in drillhole discharges at Broadlands

•		Gas;	olume p	ercent		NH ₃ (ppm) in total	Mole ratios			
Hole no.	CO_2	H_2S	H_2	N_2	HC	discharge	N_2/H_2	\overline{HC}/H_{2}	H_2S/H_2	
2*	94.2	1.6	0.17	1.8	2.25	9.9	10.4	13.2	9.3	
3*	97.4	0.94	0.054	0.62	1.0	11.8	11.4	18.3	17.4	
4*	94.5	1.1	0.25	1.45	2.72	10.1	5.8	10.9	4.4	
7*	96.6	0.81	0.22	0.86	1.4	10.7	4.0	6.7	3.7	
8*	94.8	1.57	0.23	1.14	2.32	11.2	4.9	10.1	6.8	
9	91.5	1.75	0.28	1.94	4.57	5.5	7.0	16.4	6.3	
10	96.6	0.8	0.24	0.87	1.45	1.8	3.6	6.1	3.3	
11	95.6	2.13	0.19	0.84	1.23	5.0	4.5	6.5	11.3	
12	93. 9	0.43	0.18	1.84	3.65	6.2	10.0	19.9	2.4	
13	96.4	2.82	0.041	0.27	0.51	1.8	6.6	12.2	68.0	
Wairakei										
27	90.0	4.1	0.5	2.4	2.1	1.30	4.8	4.2	8.2	
67	90.3	4.7	0.4	2.5	2.1	1.05	6.2	5.2	11.7	
Waiotapu	L									
6 Î	88.0	10.3	1.0	0.5	0.2		0.5	0.2	10.3	
7	92.2	5.3	2.0		0.5			0.25	2.6	
Kawerau	· •			,	-					
8	94.0	2.6	0.3	1.0	2.1	5.5	3.3	7.0	8.7	
10	94.6	2.5	0.1	0.9	1.9	8.0	9.0	19.0	25.0	

* Holes had a high discharge enthalpy at time of sampling.

 \overline{HC} = Total hydrocarbons, mainly methane.

ranged from approximately 36 to 395, the highest values being found on the east side of the river.

The best assessment of the gas concentration in the deep water in the undisturbed system was made from the concentration in holes which, initially at least, discharged a steam and water mixture of enthalpy similar to that of the supply water, for example, holes 2, 9, 11, 13, and 19. The average result from the five drillholes was 250 millimoles/100 moles of carbon dioxide and 5.1 millimoles/100 moles hydrogen sulfide with a CO_2/H_2S ratio of 49.3. In the castern field only hole 10 had a discharge enthalpy approximating the downhole temperature, and the carbon dioxide concentration in total discharge was approximately twice that found in the western field.

Before the Broadlands holes were discharged the downhole pressures, measured at various depth in the "liquid phase", were found to be approximately 100 to 200 psig higher than the water vapor pressure. In one particular case (hole 7) a value of 370 psig above water vapor pressure was recorded. For a carbon dioxide concentration of 250 millimoles /100 moles water to exist entirely in a liquid phase at 260° to 270°C would require that the hydrostatic pressure exceed water vapor pressure by 185 psig (Ellis and Golding, 1963). Conditions at depth at Broadlands were initially close to a state where separation of a gas-rich steam phase could occur.

Analyses of the total gases present in the Broadlands drillholes are shown in table 6. Results for drillholes at Wairakei, Waiotapu, and Kawerau are shown for comparison.

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There are no large differences between the gas composition at Broadlands and those in other geothermal areas in the Taupo Volcanic Zone. A close similarity existed between the compositions at Broadlands and Kawerau, whereas at Wairakei and Waiotapu the volume percent of hydrogen sulfide was somewhat higher and the carbon dioxide percent a little lower.

There were fluctuations in the molar gas ratios, but no obvious trends that could be correlated with depth or geology were apparent. Holes 3 and 13 (the latter hole thought to produce mainly from ignimbrite) contained relatively low hydrogen concentrations while hole 12, which was drilled into highly impermeable formations, had a rather high hydrocarbon content. There was a close similarity in gas compositions and ratios of holes 7 and 10 on the east side and those in the western sector of the field.

The partial pressures of various gases in the deep water at Broadlands were calculated (Ellis,1967) and are shown in table 7. Also listed are results from Wairakei and other geothermal fields in different parts of the world.

	TABLE 7								
Calculated	partial	pressures	of gases	iņ	underground	systems			

Area		Pressures in atmospheres								
	pCO_2	pH_2S	$^{\rm pH_2}$	pN_2	[^] pNH₃	pCH_4	Temp °C			
Broadlands †	9.0	0.1	0.11	0.95	0.0016	0.7	260			
Wairakeit '	0.9	0.02	0.09	0.02	0.0003	0.08	260			
Hveragerdi*	0.02	0.0002	0.08	0.23			216			
Larderello*	0.4	0.01	0.01	0.003	0.008		220			
The Geysers*	0.04	0.002	0.007	0.0009	0.0009		190			

+ Results are an average from several drillholes

* Results from Ellis (1967)

In most cases the partial pressures of gases at Broadlands were an order of 5 to 10 times greater than at Wairakei, the main exception being the hydrogen pressure which was similar in both areas. The higher gas content at Broadlands was thought to originate from the greater volumes of sedimentary rock in that system.

Water pH and mineral deposition.—Ellis (1970) discussed the pH of hot waters in hydrothermal systems and the influence of pH on mineral deposition. At Wairakei and Broadlands the main secondary alteration minerals controlling solution pH at highest rock and water temperatures were sodium-potassium feldspars and mica.

Hemley (1959) determined by experiment the ratio K^+/H^+ for the K-mica, K-feldspar equilibrium over a wide range of temperature. Substituting an average value of the potassium concentration in the deep 260°C water at Broadlands into Hemley's results gave a pH of 6.4. For comparison pH neutral at 260°C is 5.7. At Wairakei deep water pH's obtained by the same process of substitution were in the range 6.0 to 6.6.

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The pH of the deep water can also be estimated from the chemical analyses of the steam and water discharged from drillholes (Ellis, 1967). The complete discharge composition of individual holes is required. Estimates made from total discharge results from holes 2, 9, 11, and 19 when they were first discharged and when the enthalpies were similar to that of water at the supply temperatures gave values of between 6 and 6.2.

Browne and Ellis (1970) discussed the significance of solution pH and the concentration of carbon dioxide on the stability and presence of different minerals, particularly calcite, in hydrothermally altered rocks at Broadlands. Experimental information available on calcite solubility in salt solutions at temperatures of 200° to 300°C (Ellis, 1963, 1970) was used to show that the maximum underground pH at Broadlands which could exist before calcite was precipitated from solution was approximately 6.5. Comparison of this value with the calculated deep water value of approximately 6 to 6.4 indicated that the Broadlands waters were close to saturation with this mineral.

The high discharge enthalpy of many of the Broadlands drillholes favors the deposition of calcite within the system. The removal of steam and gas (CO_2 and H_2S) from the deep water raises the water pH allowing calcite to precipitate. Calcite was recently found to be depositing in the steel casing of hole 11, resulting in a rapid decrease in mass output of the hole from 500 to 260 k lb/hr.

Precipitates and heavy metals.—High concentrations of gold, silver, and thallium occur in antimony and arsenic sulfide precipitates, formed from springs and drillholes at Broadlands (Weissberg 1969). Analyses of arsenic in the drillhole waters gave concentrations of around 5 to 6 ppm which were generally higher than found in Ohaki Pool (1.5-3.9 ppm). The concentration of arsenic in the pool varied considerably over a monitoring period of several years. It appeared that arsenic was being transported from depth and deposited in the surface rocks and sinters. The effect of chloride concentration in controlling the concentration of these metals was recently pointed out by Ellis (1968).

The concentrations of iron and aluminum in the deep water at Broadlands, 0.36 and 0.34 ppm respectively, were approximately ten times higher than at Wairakei. Preliminary results of trace metal concentrations (Cu, Zn, Pb) in the deep waters, obtained by one of the present authors (J. B. Finlayson), showed them to be very low (0.05-4 ppb).

Isotope studies.—Preliminary isotopic studies have been made on the steam and water discharged from Broadlands drillholes. Deuterium concentrations were similar to those present in streams to the east of Broadlands but lower than the concentrations in the Waikato River or Lake Taupo water (Giggenbach, 1971). These data are best explained if the hot water at Broadlands originated from local precipitation, probably in the highlands to the east, with Waikato River-Lake Taupo waters being enriched in deuterium by evaporation.

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Lyon and Hulston (ms) calculated deep water temperatures from the C13/12 ratios in carbon dioxide and methane, on the assumption that isotopic equilibrium had been attained in the reaction $C\hat{H}_4$ + $H_2O = CO_2 + 4H_2$. From calculations used by Craig (1953) they obtained temperatures ranging from 325° to 345°C. These temperatures were higher than those obtained from Na/K ratios and silica concentrations. From the composition of the residual gases at Broadlands, Lyon and Hulston also calculated temperatures using the $CH_4 + H_2O =$ $CO_2 + 4H^2$ equilibrium. Values were similar to those obtained from the C^{13}/C^{12} ratio except for holes 11 and 13. The chemical equilibrium temperatures for these holes were 290° and 310°C, compared with the Na/K ratio temperatures of 290° and 282°C. At the time of Lyon and Hulston's survey 11 and 13 were the only holes that had discharge enthalpies similar to that of water at the supply temperatures. The remaining holes discharged a mixture enriched in steam and gas. Since the gas equilibrium method assumes that the sample is representative of the underground fluid, that is, there has been no enrichment or depletion of gas due to steam separation, the gas equilibrium temperatures calculated for holes 11 and 13 are likely to be the most accurate.

CHANGES IN DRILLHOLE CHEMISTRY WITH TIME

The changes in both water and steam chemistry of a selected number of holes at Broadlands are shown graphically in figures 2, 3, and





4. The chloride concentrations used for interhole comparison and for the present discussion are those present in the deep water. Silica supply water temperatures are shown on figure 2. The gas concentrations are given on a total discharge basis and represent the gas concentrations in the integrated mass of steam and water discharged from a drillhole.

Water chemistry.—The decreases in solute concentrations, discharge enthalpies, and supply water temperatures in many Broadlands drillholes since 1969 may have resulted from dilution, by lower temperature, lower chloride water in the system, and/or by loss of heat, originally available conductively from the aquifer rocks.

Waters of lower temperature and chloride content than the main body of hot water in the system are known to occur above and below the major aquifers at Broadlands. Ohaki Pool was originally supplied by 200°C water containing 840 ppm of chloride from a depth of approximately 305 m. Hole 20, a deep hole completed during the preparation of this paper, passed through a temperature inversion at 1065 .1 (this inversion was present in a number of other holes). The temperature and



Fig. 3. Trends in the carbon dioxide concentrations in drillholes at Broadlands between 1966 and 1970.



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chloride content of water sampled from this zone were 227°C and 720 ppm respectively.

Figure 4 shows how the chemistry of the deep water could be affected by physical changes in the system. The range of possible starting compositions of the primary hot water is shown between two large solid points in the diagram. Only one hole to date has discharged water of original temperature 267°C and chloride concentration 1150 ppm. This hole (hole 19), however, had such a large output (500 tons/hr) that the temperature was regarded as representing that present in a major upflow zone. A temperature of 262°C with a similar chloride concentration was more representative of many high production drillholes in the northwestern part of the field. Lines are drawn showing the changes that occur when the primary water is diluted.

The earliest compositions of holes 7, 10, and 20 fall close to the line corresponding to dilution of 267°C water with the colder water that occurs at depth in hole 20. In the formative stages of the B sadlands system, it seems possible that water from the western part of the field, at 267°C and containing 1150 ppm chloride, flowed out to the southeast, undergoing dilution in transit.

During exploitation the chemistry of the eastern holes have shown little permanent change. Fluctuations of the chloride concentration in hole 7 could be caused by evaporation on rock surfaces. Increasing supply water temperatures in holes 7 and 10 and decreasing values in hole 14 indicate that transfer of heat between rock and water by conduction could be important. These trends suggest that the eastern holes are producing from porous medium rather than fractures or faults.

The early compositions of the discharges of many of the western holes suggest a rather complex history of water migration before and during production. Waters at holes 3, 4, 8, 11, 17, and 18 appear to have been concentrated by both boiling and evaporation on rock surfaces. With the exception of hole 4, the average trend for these holes after 2 years corresponds to dilution. The trend line for hole 4 suggests loss of heat by conduction, but the slope of short term changes is probably explained by evaporation on rock surfaces combined with dilution.

The initial water discharged from hole 13 had lost heat conductively. Under exploitation conductive heat loss as well as boiling was apparent. The initial water composition and temperature of hole 1 suggested that the water reaching the northeast of the field had lost steam by boiling.

Since the beginning of 1970 the rate of fall of chloride concentrations and temperatures in most holes decreased, and in some cases, for example, in holes 8 and 11, values became constant. The apparent stable values attained by several of the drillholes were above those assumed to be present in the diluting water and could thus represent only a temporary condition. However it may also mark a limit to the extent of inflow of diluting water. The chemistry of the Broadlands geothermal area New Zealand 67

TABLE 8

Changes in the ratio of Na/K in drillholes over the discharge period

Hole no.	Date	Na/K	Temp°C	Date	Na/K	T°C
2	23. 8.66	8.0	288	7 4 70	0.9	0.00
3	28. 4.67	8.3	281	25 3 70	5.5 12.0	202
4	6. 9.67	8.4	280	16, 2.70	9.5	240
7	14. 5.67	.9.4	261	28.11.69	9.5	200
8	29. 2.68	7.5	· 300	20. 4.70	89	200
9	14. 5.68	7.8	293	24. 4.70	8.1	286
10	18.10.68	10.85	240	24. 7.69	9.8	268
11	22. 8.68	7.9	290	28, 4.70	9.0	268
13	10.10.68	8.3	282	4. 5.70	7.9	290

Changes of the Na/K ratios and chemical equilibration temperature are shown in table 8.

With the exception of holes 7, 10, and 13 the Na/K ratios have increased in the discharges of holes that have decreased in chloride concentration and temperature. The temperature corresponding to equilibration at the new values did not correspond closely with the silica temperatures, variations being of the order of 10° to 30°C. It is possible that the high gas content at Broadlands influences the Na/K ratios.

Gases.—Changes in gas concentrations (carbon dioxide and hydrogen sulfide) in drillholes can be correlated with changes in discharge enthalpies (fig. 3). Increasing gas concentrations occurred in holes that increased in steam fraction. The CO_2/H_2S ratios also increased indicating that the added steam was derived from water boiling close to the production zones.

In recent months decreasing supply water temperatures have been accompanied by decreasing discharge enthalpies and gas concentrations. The gas concentrations, in total discharge, however, have not failen below the value present in the deep water, nor have the enthalpies decreased to the temperatures of the supply water.

The trends in gas concentrations at Broadlands are similar to those seen for high enthalpy drillholes at Wairakei, (Mahon, 1962a; Ellis, 1962; Glover, 1970). With the present pressure and temperature trends in the system it is apparent that carbon dioxide and hydrogen sulfide concentrations and the ratio CO_2/H_2S will decrease with time (Ellis, 1962).

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ABSTRACT, Korzl in light of chromato process is identical Shape and velocity column depend on tion of component i vex to the C_{L1} axis fronts. The velocity $dC_{1,f}/dC_{1,s}$. The velthe chord connecting

The theory is equilibria, Infiliratio sults in a leading d followed by a self-sh centage Or at which Na) ratio of the infil

Extension of the component gives rise be caused by solubili

The presence of rather than diffusion in one direction only plateaus in solid soli sharp front; and the ments such as Li, Be placement fronts.

The study (theoretical work proach has been concept of local (that is useful in 1959; Thompson. transport equation in a "metasomatic treatment has so ture, even though formation beyond Korzhinskii (

cal work on meta transport equation extreme types of n "material is trans!

¹ This approach 1 by Korzhinskii (1966, ments discussed in the of local equilibrium is

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