

CHEMICAL TECHNIQUES IN GEOTHERMAL EXPLORATION

W.F. GIGGENBACH

Chemistry Division, DSIR, Private Bag, Petone, New Zealand

INTRODUCTION

The application of chemical techniques has become an integral part of any geothermal exploration programme. Especially during the early, pre-drilling stages, geochemistry may provide information on deep conditions and processes not obtainable by geological or geophysical techniques. After all, the waters and gases discharged at the surface "have been there" and generally carry imprints of their deeper histories with them. The constituents encountered in these fluids may be subdivided into two major groups according to the type of information provided:

Chemically inert, non-reactive constituents form a group which may be called *tracers*. Once added to the fluid phases, ideally they should remain unchanged, providing a tag allowing their origins to be traced back to their source components.

Chemically reactive species, responding to changes in their environment in a controlled and well understood manner, form a group potentially useful as *geoindicators*.

Examples of the first group are, of course, the noble gases He and Ar, followed by the comparatively "conservative" constituents Cl, B, Li, Rb, Cs, and N₂. The species of the second group, such as Na, K, Mg, Ca, and SiO₂, take part in temperature-dependent interactions with the Al-silicate rock structure generally housing geothermal systems, or are, as e.g. H₂, H₂S, CH₄, and CO₂, involved in temperature- and pressure-dependent redox reactions among one another or with redox systems (FeII/FeIII) of the rock phase. The boundaries between the two groups are not rigid. A constituent may under one set of conditions be quite inert, e.g. Cs at temperatures > 250°C, but it is incorporated into secondary zeolites at lower temperatures. Each of the constituents of geothermal fluids behaves in its own peculiar way and therefore, if used to best advantage, will provide unique information.

In this introduction to the application of chemical techniques in geothermal exploration, simple procedures are described allowing an initial assessment of the geothermal potential of an area to be made by extracting much of the information carried by a given constituent in a comparatively straight-forward manner. The procedures frequently require an initial, "eyeball" assessment of correlations among sets of various constituents, a task most readily carried out by use of triangular diagrams. A special effort, therefore, is made to point out the peculiarities of this type of data presentation. The procedures are based on constituents analyzed most frequently and by readily available techniques (Giggenbach and Goguel, 1989).

Sets of analytical results for quite arbitrarily selected water and gas samples, spanning a wide range of tectonic, geological and hydrological environments, are given in Tables 1 and 2. For four high temperature geothermal areas (WK, NG, ZU, and MV), pairs of samples representing well and associated spring or fumarole discharges are given. The two El Ruiz samples are from a highly acid volcanic spring and a neutral chloride spring at lower levels. The Araro samples are likely to represent the natural outflow of chloride water from the Los Azufres geothermal field. The two samples from boiling springs at Manikaran and Fang have no obvious volcanic-magmatic associations; the Yasur water is discharged from the complex housing the active volcano, the gas sample from an associated "geothermal" fumarole. The Paraso samples are from an extensive area of hot water discharges on this volcanic island; the Lake Nyos samples represent the deep, CO₂ charged waters there. The Waitangi Soda Spring samples are also produced from a highly CO₂ charged system. MO and MU are associated with natural gas discharges along the east and west coast of New Zealand, while the White Island samples are from a spring producing highly acidic, obviously volcanic waters.

These data will be used as examples to illustrate the various procedures. Conclusions drawn here should in no way be considered prejudicial to any ongoing or future investigations.

Table 1

The chemical composition of thermal and mineralized waters from New Zealand (WK, NG, MO, MU, We), Guatemala (ZU), Costa Rica (MV), Colombia (RA, RB), Mexico (AR), India (MA), Thailand (FN), Solomon Islands (PR), Vanuatu (YA) and Cameroon (LN) in mg/kg.

Area	°C	pH	Li	Na	K	Rb	Cs	Hg	Ca	B	HCO ₃	SiO ₂	SO ₄	Cl
WK Wairakei, well	240	8.5	10.7	1170	167	2.20	2.00	0.01	20	26	5	590	35	1970
WK Wairakei, spring	99	7.7	14.5	1220	140	2.30	2.10	4.50	30	43	30	320	30	2100
NG Ngawha, well	230	7.1	10.9	880	75	0.30	0.75	0.10	3	895	310	385	26	1240
NG Ngawha, spring	80	7.2	10.4	910	64	0.29	0.60	1.40	11	850	330	150	446	1290
ZU Zunil, well	300	8.4	8.1	1030	210	1.90	2.00	0.01	11	45	150	890	61	1700
ZU Zunil, spring	87	8.7	0.6	260	37	0.08	0.02	43.0	43	5	500	200	195	170
MV Miravalles, well	245	7.5	5.7	1970	238	1.05	0.60	0.02	73	54	40	590	36	3300
MV Miravalles, spr.	73	8.5	3.4	1970	79	0.21	0.14	6.50	22	48	910	112	120	2600
RA Ruiz, acid spring	62	1.2	0.3	280	224	0.37	0.04	155	214	8	-	154	10670	1350
RB Ruiz, neutral s.	94	8.0	3.8	610	78	0.56	0.62	5.1	48	19	175	180	41	1000
AR Araro, spring	92	8.1	6.6	705	50	0.43	1.12	0.3	30	75	63	230	135	1010
MA Manikaran, spring	94	7.4	1.2	93	21	0.15	0.14	3.3	51	3	190	75	35	130
FN Fang, spring	99	9.0	0.6	122	8	0.14	0.29	0.1	1	<1	145	195	22	27
PR Paraso, spring	56	5.6	1.8	1210	178	0.74	0.09	26.6	289	16	6	150	205	2340
YA Yasur, spring	99	8.8	0.3	1270	73	0.16	0.01	0.3	17	21	75	270	280	1690
LN Lake Nyos, lake	23	5.4	.01	15	5	.004	.001	35.0	30	<1	400	45	<1	<1
WS Waitangi Soda Spr.	49	7.3	1.7	285	24	0.11	0.07	8.9	17	3	265	176	48	365
MO Morere, spring	47	7.0	4.6	6700	84	0.10	.004	80.0	2360	57	30	27	<3	15800
MU Maui, well	130	7.5	3.6	7880	440	0.71	0.08	48.0	190	15	630	36	18	12600
WI White Isl. spring	98	0.6	2.9	5910	635	5.40	0.36	3800	3150	160	<1	-	4870	38700
SW Seawater	4	7.8	0.2	10560	380	0.13	<.01	1270	400	5	140	-	2710	19000

Table 2 The chemical composition of gases associated with the water discharges of Table 1, on water-free basis in mmol/mol.

Area	°C	CO ₂	H ₂ S	He	H ₂	Ar	H ₂	CH ₄
UK Wairakei, well	240	885	100	0.0080	2.400	0.180	8	2.5
UK Wairakei, fumarole	104	975	7	0.0220	1.600	0.300	14	2.8
NG Ngawha, well	230	950	10	0.0050	2.800	0.004	3	25.0
NG Ngawha, pool	80	900	4	0.0110	7.100	0.020	8	60.0
ZU Zunil, well	300	960	25	0.0020	4.300	0.060	8	0.2
ZU Zunil, fumarole	87	930	36	0.0045	6.440	0.200	25	1.3
MV Miravalles, well	245	980	6	0.0015	3.300	0.050	8	0.3
MV Miravalles, vent	98	983	9	0.0025	1.200	0.020	3	3.1
RA El Ruiz, spring	62	928	26	0.0018	<.010	0.790	48	1.8
RB El Ruiz, spring	94	933	40	0.0005	0.060	0.350	25	3.0
AR Araro, spring	92	957	1	0.0030	0.012	0.660	37	0.2
MA Manikaran, spring	94	985	5	0.1800	0.013	0.180	7	0.7
FN Fang, spring	99	750	200	0.0210	1.800	0.600	21	4.8
PR Paraso, spring	56	974	2	0.0110	4.420	0.030	3	2.1
YA Yasur, fumarole	99	780	86	0.0008	72.000	0.800	53	0.6
LN Lake Nyos, diss. gas	23	996	<1	0.0040	0.0002	0.050	2	2.0
WS Waitangi Soda Spring	49	980	<1	0.0042	0.002	0.550	22	1.1
MO Morene, spring	47	3	<1	0.0360	0.020	0.540	12	920.0
MU Maui, gas well	130	150	<1	0.2100	<.001	0.180	40	850.0
WI White Island, pool	98	840	100	0.0030	1.100	0.050	20	8.0

CONSTITUENTS PARTITIONING INTO THE LIQUID PHASE

Relative Cl, SO₄ and HCO₃ contents

Most geochemical techniques may with confidence be applied only to specified types of fluids with limited ranges of compositions. For instance, most ionic solute geothermometers "work" only if used with close to neutral waters containing chloride as the major anion. Any such interpretation of geothermal water samples, therefore, is best carried out on the basis of an initial classification, e.g. in terms of their major anions Cl, SO₄ and HCO₃, as shown in Fig. 1.

The position of a data point in such a triangular or trilinear plot is simply obtained by first forming the sum S of the concentrations c_i (in mg/kg) of all three constituents involved. In the present case

$$S = c_{Cl} + c_{SO_4} + c_{HCO_3} \quad (1)$$

The next step consists of the evaluation of "%-Cl" and "%-HCO₃" according to

$$\text{"%-Cl"} = 100c_{Cl}/S \quad (2)$$

and

$$\text{"%-HCO}_3\text{"} = 100c_{HCO_3}/S \quad (3)$$

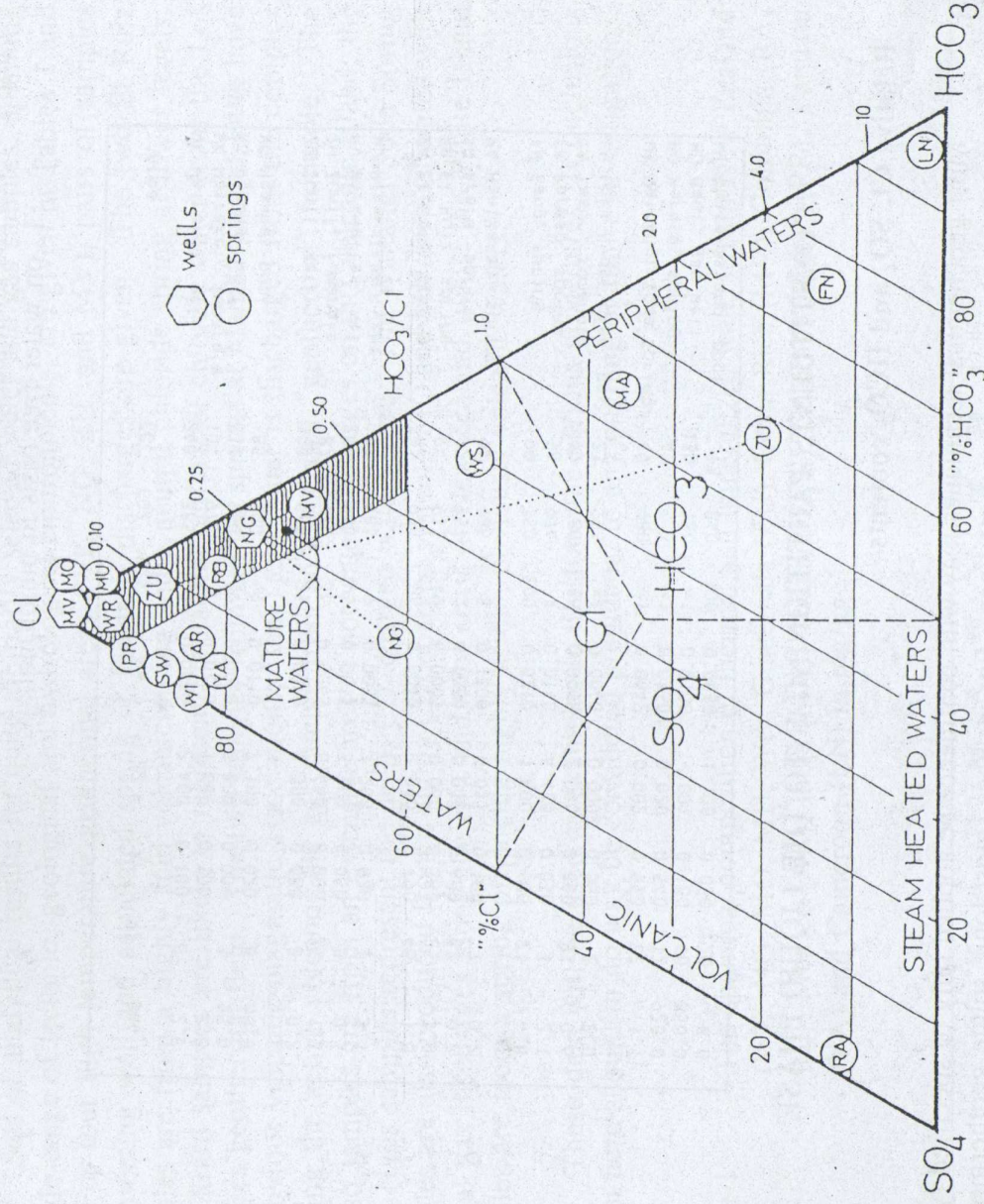


Figure 1 Relative Cl, SO_4 and HCO_3 contents of thermal waters on weight (mg/kg) basis. For symbols see Table 1.

Not much is gained by converting concentrations by weight (mg/kg) first to molar concentrations (mol/kg). Conversion to molar concentration units is only required in the application of more sophisticated thermodynamic techniques.

Presentation of data in terms of such triangular diagrams has the advantage that none of the constituents is "prejudged" as is the case by plotting e.g. ratios where the constituent in the denominator assumes the role of a normalizing factor and can e.g. not be zero. In contrast to logarithmic plots, mixing lines in triangular diagrams remain always straight lines. The diagrams also allow the immediate "eyeball" statistical evaluation of groupings and trends. It should, however, be kept in mind that any such three-component plot tells only part of the story and that some apparent correlations may only be purely accidental. The close proximity of the data points for the White Island brine (WI), seawater (SW) and the Araro thermal spring (AR) in Fig. 1 may suggest, but in no way proves, a close genetic relationship among them. Correlations indicated by one set of components have to be checked by use of additional independent data.

In many ways the triangular diagrams used here resemble the popular diagram proposed by Piper (1944) some 45 years ago for the classification of natural waters. Its major disadvantage is the use of sums of constituents thus obliterating any information carried by an individual constituent. Also, the interpretative value of these diagrams is only minimal if applied to geothermal waters. They are usually only presented as such and do not appear to encourage further or deeper discussion of source components, formation processes or thermodynamic correlations.

In Fig. 1 compositional ranges are indicated for several typical groups of thermal waters such as volcanic and steam-heated waters formed by the absorption of high temperature, HCl-containing volcanic, or lower temperature, H_2S -containing "geothermal" vapors, into groundwater. Most geochemical techniques are not suitable for application to these generally quite acid waters. The group best suited comprises the neutral, low sulfate, high chloride "geothermal" waters along the Cl-HCO₃ axis, close to the Cl corner. In the case of albeit neutral, but high bicarbonate waters, considerable caution is required in the application of most "geoindicators".

Fig. 1 not only allows the weeding out of unsuitable waters, but may already provide an initial indication of mixing relationships or geographic groupings, with e.g. Cl waters forming a central core grading into HCO₃ waters towards the margins of a thermal area. High SO₄ steam-heated waters are usually encountered over the more elevated parts of a field. The degree of separation between data points for high chloride and bicarbonate waters gives already an idea of the relative degrees of interaction of the CO₂ charged fluids at lower temperatures, and of the HCO₃ contents increasing with time and distance travelled underground.

This interpretation is supported by the shift in the position of data points representing spring discharges to higher relative HCO₃-contents as compared to the well discharges at Ngawha (NG), Miravalles (MV) and especially Zunil (ZU). The compositional area where ionic solute geoindicators may be applied with sufficient confidence is quite small (hatched area in Fig. 1) and illustrates the need for this initial classification procedure.

Relative Li, Rb and Cs contents

The distribution of data points in Fig. 1 stresses differences among waters, largely brought about by comparatively shallow processes. An indication of the existence of a common origin, or of common, deep processes shaping the composition of surface water discharges, is provided by use of less reactive, "conservative" components, added at depth, but not affected by shallow processes, such as the rare alkalis Li, Rb and Cs.

Relative Li, Rb and Cs contents of Fig. 2 again are plotted in terms of a trilinear diagram. Because of the large differences in the analytical values for the three components, normalizing or scaling factors had to be applied to achieve an even spread of data points over the plot. Omission of these scaling factors would have led to "bunching" of points in the Li corner of the plot.

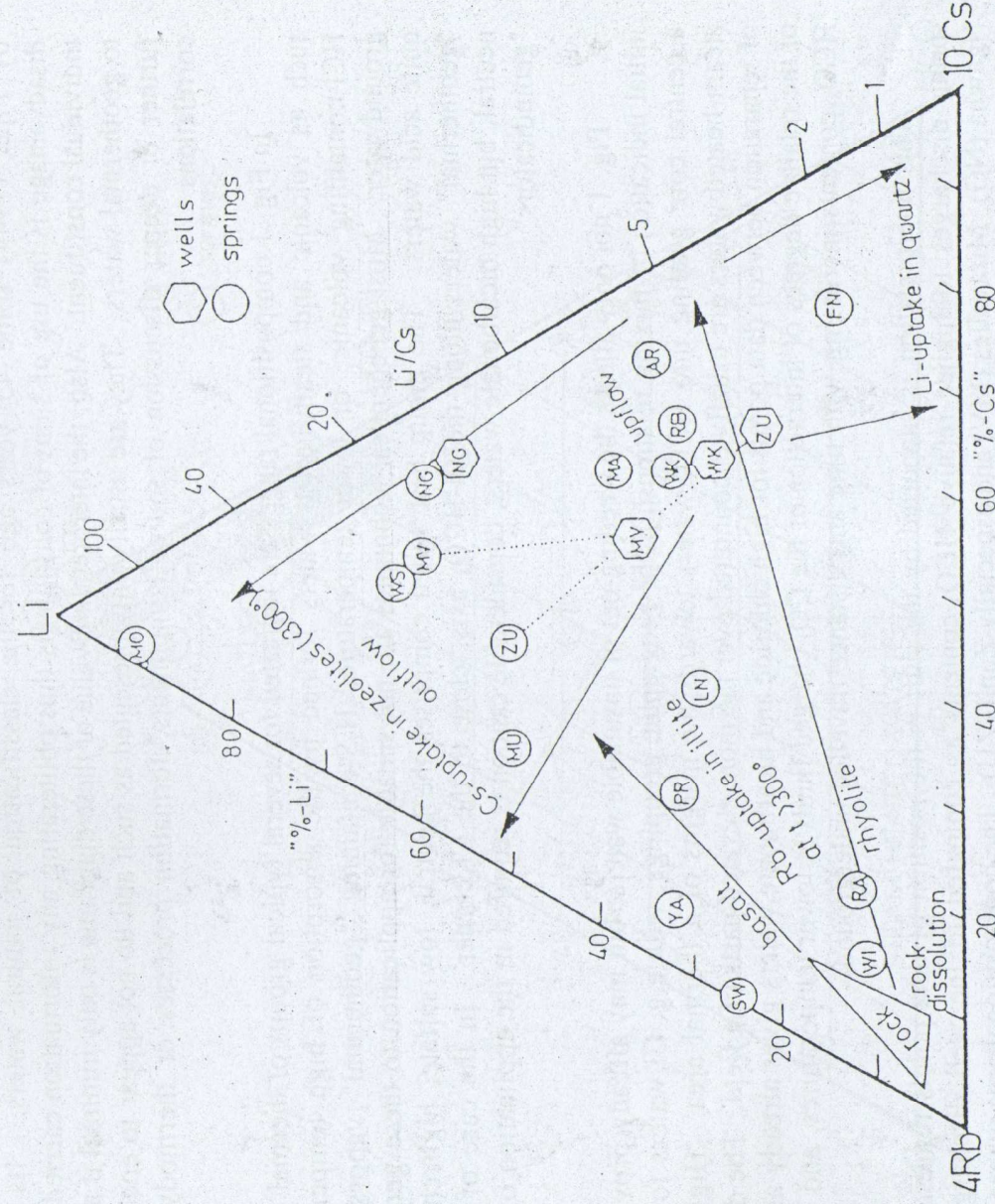


Figure 2 Relative Li, Rb and Cs contents in the thermal water discharges on weight basis.

The numerical value given to these scaling factors depends on the choice of constellation of data points to be given special attention. Generally speaking, triangular diagrams can only cope with a spread of values for a given variable over two orders of magnitude. Any data points representing values outside this range are bunched along one of the axes with considerable loss of detail or resolution. By varying the scaling factors, different groups of data points can be shifted into the center of the diagram where resolution is highest; in other words they can be put under the magnifying glass. No matter which linear scaling factors are chosen, mixing lines always remain straight.

Coordinates for Fig. 2 were calculated according to

$$S = c_{Li} + 4c_{Rb} + 10c_{Cs} \quad (4)$$

$$\text{"%-Li"} = 100c_{Li}/S \quad (5)$$

$$"%-Cs" = 1000c_c/S \quad (6)$$

In the application of this triangular plot, advantage is taken of its insensitivity to dilution by little mineralized ground water or steam loss due to boiling of the rising fluids. Because of this, data points for deep and shallow waters, having undergone any amount of dilution or steam-loss, plot on the same position. The presentation also allows the composition of average crustal rocks from basalts to rhyolites to be shown.

Water-rock interaction in geothermal systems with close volcanic-magmatic associations may be described in terms of two somewhat hypothetical, but well-defined endmember processes (Giggenbach, 1988):

Initial *dissolution* of crustal rocks in acid waters formed e.g. through absorption of magmatic vapors into deeply circulating groundwater. The waters formed in this "fluid-dominated" alteration process contain most of the more soluble rock constituents in proportions close to those of the original rock. The rock phase resulting from this process is heavily depleted in the more easily leached components.

Final *equilibrium* of the fluid phase with "the rock" in its thermodynamically stable mineral configuration formed through recrystallization of the original, thermodynamically unstable primary rock. The chemical composition of this secondary, stable rock phase closely approaches, or is the same (isochemical) as that of the original rock. This process is likely to come to completion only in stagnant systems of infinite age. The composition of the fluids in such "rock-dominated" alteration systems, however, is for a wide range of Al-silicate rocks uniquely fixed and essentially only a function of temperature and salinity (chloride content).

The compositions of waters, gases and rocks in actual, dynamic hydrothermal alteration systems can be expected to correspond to the attainment of some steady state, intermediate between these two endmember processes. By comparing the compositions encountered in thermal fluid discharges with these theoretical compositions, however, it is possible to assess the relative importance of the two processes in shaping the composition of a given discharge and of other processes active at depth within a geothermal system.

The data points of the waters in Fig. 2 are generally far removed from the compositional area of crustal rocks, pointing to the existence of a number of secondary processes affecting even these three "conservative" constituents during their rise to the surface. In a detailed study of the behaviour of rare alkali elements during hydrothermal alteration in New Zealand's geothermal systems, Goguel (1983) found that Rb closely paralleled K in that it is already taken up at quite high temperatures ($> 300^\circ$) in most K-containing alteration products, such as illite. Cs is incorporated into secondary zeolites, especially at temperatures $< 250^\circ$. Li is to minor degrees incorporated into secondary quartz and chlorite. Comparison of fresh and altered andesite and rhyolite in drillcores from these systems showed that the rare alkali metals have actually been added during rock alteration rather than leached, or in other words that they must have been dissolved from rock well below drilled depth.

The only waters with compositions close to those of crustal rocks are the two highly

acidic waters from White Island (WI) and Aguas Calientes (RA), indicating rock dissolution. All neutral waters have obviously lost Rb due to uptake in illite, shifting data points away from the Rb corner. Li/Cs ratios, especially of well discharges, are still close to those of the original rock. The increase in Li/Cs for spring discharges suggests removal of Cs through incorporation into zeolites at lower temperatures. The relative position of data points and the delineation of trends, therefore, allows e.g. the assessment of the position of thermal water discharges with respect to upflow (low Li/Cs) and outflow (high Li/Cs), and of relative degrees of water-rock interaction at high temperatures or acidities. Li/Cs ratios are also a function of rock type, lower in acid rocks as compared to basalts (Taylor, 1964).

Relative Cl, Li and B contents

The alkali metal probably least affected by secondary processes is Li. It may, therefore, be used as a "tracer" for the initial deep rock dissolution process and as reference to evaluate the possible origin of the other two important "conservative" constituents of thermal waters, Cl and B. Fig. 3 shows their relative contents for the wide variety of thermal waters listed in Table 1.

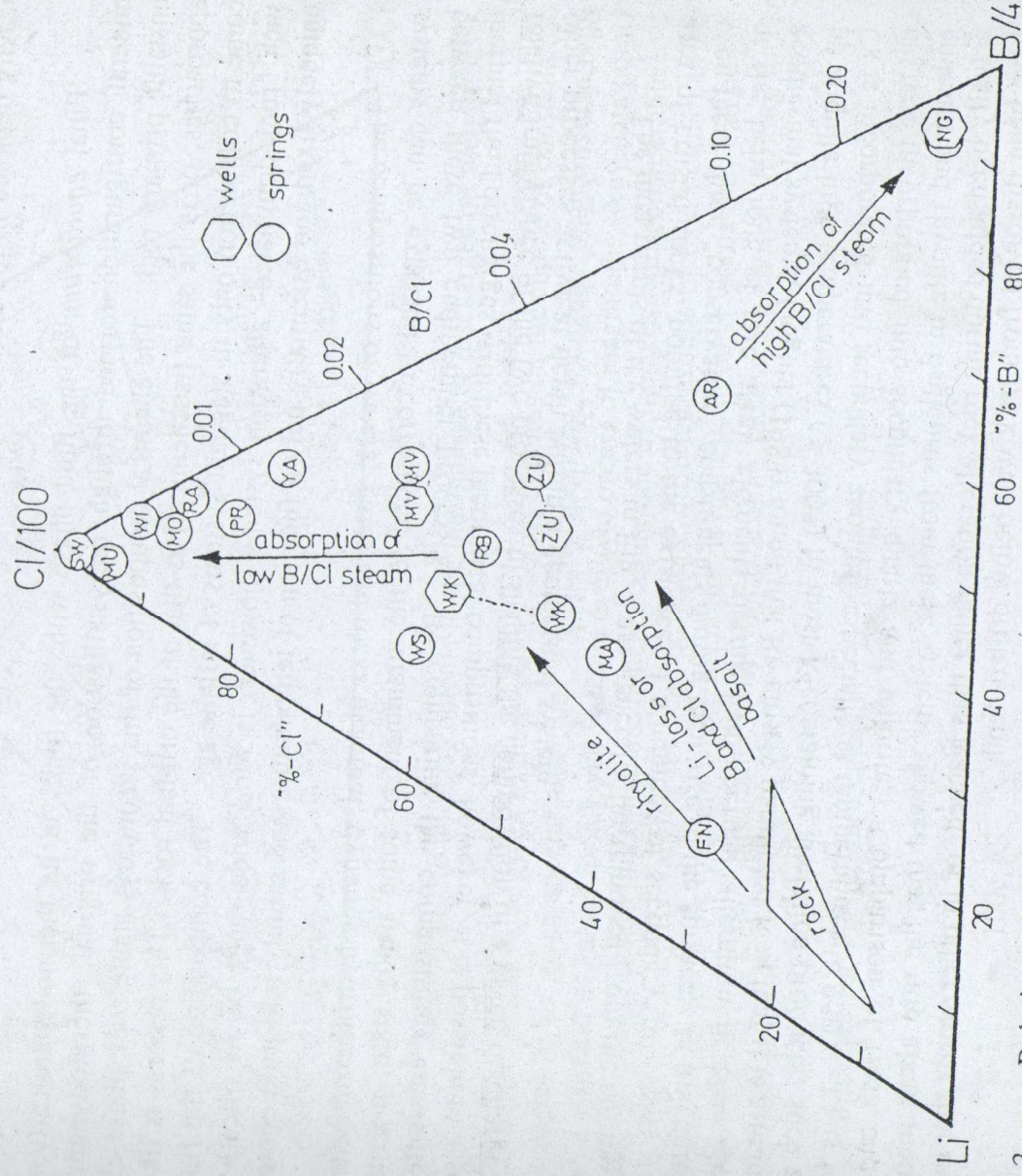


Figure 3 Relative Cl, Li and B contents in thermal waters on weight basis. For symbols see Table 1.

Of all these, only the very low chloride water, discharged at Fang, plots close to the composition of crustal rocks, suggesting that its composition may be due to simple rock leaching. Relative Cl and B contents for all others are much higher suggesting either addition of these two elements before, during or after the rock dissolution process, or loss of Li. The latter is quite unlikely as there is no obvious major sink for this element in hydrothermal systems. Once added, Li remains largely in solution. It is, however, striking that both Cl and B are added to the Li containing solutions in proportions close to those in crustal rocks. At high temperatures Cl occurs largely as HCl, and B as H_3BO_3 . Both are volatile and able to be mobilized by high temperature steam. They are, therefore, quite likely to have been introduced with the magmatic vapors invoked above to lead to the formation of the deep acid brine responsible for rock dissolution. At lower temperatures the acidity of HCl increases rapidly, and it is soon converted by the rock to less volatile NaCl; B remains in its volatile form to be carried in the vapor phase even at lower temperatures.

The distribution of data points for most of the geothermal systems with close volcanic-magmatic associations, such as Wairakei (WK), Miravalles (MV) and Zunil (ZU) in Fig. 3 then may be explained in terms of dissolution of rock in waters formed through absorption of high temperature, high pressure magmatic vapors in deeply circulating groundwaters. These vapors may contain Cl and B in proportions close to those of the rock contacted. Data points close to the Cl corner either represent waters formed through absorption of, in this case, low B/Cl magmatic vapors, or waters affected by the admixture of low B/Cl seawater (SW, MU, MO). Absorption of high B/Cl steam, after neutralization of HCl, is indicated for Araro (AR) and especially Ngawha (NG). The B content of thermal fluids is likely to reflect to some degree the maturity of a geothermal system. Because of their volatility, constituents such as B, As, Sb and Hg are likely to be expelled during the early heating up stages. Fluids from "older" hydrothermal systems can be expected to be depleted in these elements.

In spite of being affected to some degree by secondary chemical processes, the above five constituents Li, Rb, Cs, B and Cl provide very useful markers for the identification of, and tracers to the origins of geothermal fluids. The remaining constituents listed in Table 1, Na, K, Mg, Ca and SiO_2 , are chemically more reactive and form the basis for a number of valuable geindicators.

The Na-K-Mg-geothermometer

Ionic solute geothermometers such as those based on Na-K- (Ellis and Mahon, 1967) and Na-K-Ca-contents (Fournier and Truesdell, 1973) provide powerful tools for the evaluation of deeper conditions within geothermal systems. Most of the problems in their use arise from their application to unsuitable samples. Initial weeding out on the basis of pH or their relative Cl, SO_4 and HCO_3 contents, (Fig.1), goes a long way to improve their reliability. Recently a "self-policing" technique was devised giving an automatic indication as to the suitability of a given water for the application of ionic solute geindicators (Giggenbach, 1988). It is essentially based on the temperature dependence of the two reactions.

