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BORON DISTRIBUTION BETWEEN LIQUID AND VAPOUR IN GEOTHERMAL FLUIDS

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ABSTRACT

One of the major causes of change in the chloride/boron ratio across a geothermal reservoir is the volality of boron.

Analysis of boron in separated steam and water from fluids discharged by Wairakei and Ohaaki-Broadlands wells together with some published data have enabled the relationship of boron distribution between vapour and liquid with temperature to be defined.

log (boron in vapour/boron in liquid) = -0.947 x log (density of liquid/density of vapour) + 0.0547 (density of liquid/density of vapour) .

While volatility of boron can explain the creation of shallow boron rich waters, other mechanisms are needed to explain the formation of boron deficient waters.

INTRODUCTION

Boron in Geothermal Fluids

One of the parameters used to follow the history of geothermal fluids is the Chloride/Boron ratio and this has been used to characterise different reservoirs. The ratio in the water is similar to that in the parent rocks (Ellis and Sewell, 1963). Greywacke is a relatively abundant source of boron, and contains little chloride. Thus the water at Ngawha (a greywacke reservoir) has a Cl/B mole ratio of less than 1. Cl/B ratios in East and West Broadlands are 6 and 12 respectively reflecting the deeper greywacke in the latter area.

However, changes in Cl/B occur as the fluids move through the geothermal reservoir, e.g. the deep water at Mahiao (Philippines) has a Cl/B of 14, and the outflow springs in the Bao Valley have ratios about 30 indicating a loss of boron from the water relative to chloride (Lovelock et al 1982). Chloride is regarded as a conservative ion i.e. once it is in the geothermal liquid it is not removed either by adsorption into or reaction with the host rock, or by mineral formation, or by volatility in the steam phase. Boron is known to partition into the steam phase, especially at high temperatures.

A second mechanism for boron loss is by adsorption on to clay minerals, principally illite, Harder, 1961 and Couch and Grim, 1968.

PREVIOUS WORK

Volatility of Boron

Van Stackelburg et al (1937) and Jaulmes and Galhac (1937) reported the partial pressure of boron in steam and the concentration of boron in superheated steam after it was passed through boric acid at atmospheric pressure and at temperatures up to 180°C and up to 210°C respectively. They also noted that a change in the crystalline phase occurred between H_3BO_3 and HBO_2 at 140 to 144°C.

Van Stackelburg et al (1937) and Jaulmes and Gontard (1937) measured the distribution of boric acid between steam and water at atmospheric pressure and at 101.6 and 100°C respectively.

Styrikovich et al (1960) were the first workers to relate the distribution coefficient (K_D) to the temperature using the density of steam (d_v) and density of water (d_l);

$$K_D = B_v/B_l = (d_v/d_l)^{0.885} \qquad (1)$$

or

$$\log K_D = -0.885 \log (d_l/d_v) \qquad (2)$$

where K_D = mass concentration of boron in vapour, B_v /mass concentration of boron in liquid, B_l.

Byrnes (1962), reported in Cohen (1969), measured K_D in pure boric acid solutions and in partially neutralised boric acid solutions, and assumed that the volatility was all due to the undissociated boric acid.

Tskhvirashvili and Galustashvili (1964) reported B_v/B_l values from 249 to 363°C. By changing the pH they separated the K_D values for the unionised and ionised borate, the latter value being 20-30% of the former.

Tonani (1970) used data from Jaulmes and Gontard (1937) and Nasini (1930) to obtain a relationship between K_D and 1/T (°K), the approximate equations to the two parts of Tonani's 1970 curve are;

$$\log K_D = 7.751 - \frac{3788}{t + 273.15} \quad [100°C < t < 141°C] \qquad (3)$$

and

$$\log K_D = 0.1899 - \frac{657}{t + 273.15} \quad 141°C < t < ? \qquad (4)$$

Tonani (pers. comm.) has also used a broad average curve based on previous data.

$$\log K_D = 2.81 - \frac{2088}{t + 273.15} \quad 100°C < t < ? \qquad (5)$$

Ellis and Mahon (1977) used data from Wilson (1974) who is quoting data from Cohen, together with data from Wairakei supplied by the present author (see later), and Styrikovich et al (1960) to plot -log K_D v temperature (°C). Their tabulated value are taken from equation (1) above.

PRESENT WORK

Sampling Methods

The steam and water fractions of a two phase geothermal fluid were separated using a 2" two stage Webre cyclone separator. The stainless steel unit consists of two Webre separators (Pollak and Work, 1942) operating in series as described by Ellis and Mahon, 1977. Mahon (1961) outlined the routine procedures used for sampling geothermal wells and detailed the positions of sampling points on the surface discharge pipes from which representative steam and water samples are obtained. Sample points on the Wairakei wells used in 1962 conformed with the specifications of Mahon. Later changes in pipe configuration designed so that the wellhead pipework and silencer is accommodated on a smaller site may result in sample points in less desirable locations. This can result in less efficient separation (see below).

Separated water was collected through a cooling coil incorporated in the separator into a 500 ml or a 1 litre plastic bottle. A sample of water was also collected at atmospheric pressure from the weirbox of the silencer. Separated steam was collected through a cooling coil immersed in cold water into a 500 ml or 1 litre plastic bottle. Alternatively, the steam was collected into a large (5 to 12 litre) evacuated flask and condensed by a spray of cold water on the outside of the flask.

Wells Sampled

In 1962 samples were collected from wells at Wairakei, i.e. WK21, WK27, and WK205 (see also Ellis and Mahon, 1977), at temperatures between 132 and 201°C. In 1976, well BR25 at Ohaaki-Broadlands, was sampled at nine different separation pressures, equivalent to separation temperatures from 149 to 258°C. Finally, in 1987, well BR45 at Ohaaki-Broadlands was sampled at six pressures equivalent to 125 to 241°C.

Analytical Methods

A. Boron

1. Water samples were analysed by the mannitol method (Foote, 1932). The pH of the solution (100 mis) was adjusted to 7.3. Addition of mannitol forms an acid complex which was titrated with 0.025 N sodium hydroxide.

2. Steam samples. Those collected in 1962 were concentrated approximately 10 fold by evaporation after addition of sodium hydroxide to bring the pH to greater than 11. The final solution was analysed by the mannitol method. Later steam samples were analysed directly using Azomethine-H. This method had the advantage of using a 15 ml aliquot containing 0-2 mg B/litre (BWS, 1980).

B. Chloride

Water samples were titrated against 0.1 N silver nitrate solution using potassium chromate as indicator (A.S.T.M., 1966). Sulphide was removed from the samples by acidification and bubbling with nitrogen. The solution was then neutralised with calcium carbonate before titration. Steam samples were treated with sodium hydroxide to raise the pH to above 11 then heated on a water bath with hydrogen peroxide to oxidise the sulphide. After cooling the solution, a 100 ml aliquot was titrated with 0.002 M silver nitrate to a potentiometric end point using a Metrohm (R) Automatic Titrator.

Efficiency of Separation and Corrections

The concentration of chloride detected in the steam condensate can be used to calculate water contamination of the steam phase. As the chloride/boron ratio of the water in the total fluid is known a correction can be applied to the analysed value of boron for that carried over in the water phase.

Similarly, dilution of the liquid phase chloride is evidence for contamination by steam. As the boron distribution is heavily in favour of the water phase, contamination of steam by water is much more serious than the contamination of water by steam. To correct for the latter, boron concentration in a sample collected at atmospheric pressure and the discharge enthalpy of the well were used to calculate the boron in the total discharge from the well. Then the boron concentration in the water separated at higher pressures was calculated from the total discharge concentration assuming no partition into the steam. If this value was more than 5% greater than the analysed value then the calculated value was used. This was only the case in three low pressure BR45 samples where gross dilution was observed.

Results

Table 1 shows Sample No., Well, date, sampling pressure (in bars absolute), equivalent temperature of separation (in °C), the boron and chloride concentrations in the steam (in g/tonne), the boron correction to the analysed boron in the steam and the corrected boron concentration in the steam (in g/tonne), and the analysed and corrected boron

TABLE 1: Boron Volality Data

Sample No.	Well	Date	Sampling Pressure Ba	Temp. °C	Analysed B in Steam (g/t)	Analysed Cl 1n Steam (g/t)	B Correction	Corrected B In Steam (g/t)	Analysed B 1n Water (g/t)	Corrected B in Water (g/t)	K_D	$1/K_n$	Log K_n	Log d_r/d_v	
836	WK27	11/04/62	15.83	201.0							.0240	41.7	-1.6198	2.0325	o
837	WK21	"	7.55	168.0							.0115	87.1	-1.9393	2.3594	o
962	WK205	14/11/62	2.86	132.1	.227			.227	26.17	26.17	.0087	115.29	-2.0618	2.7719	o
963	"	15/11/62	5.21	153.5	.179			.179	18.15	18.15	.0099	101.40	-2.0060	2.5180	o
964	"	"	5.97	158.7	.143			.143	18.35	18.35	.0078	128.32	-2.1083	2.4598	o
3665	BR25	9/11/76	25.83	225.7	1.55	7.43	.25	1.30	37.0	37.0	.0351	28.46	-1.4543	1.8096	+
3666	"	10/11/76	29.97	249.5	1.79	.63	.02	1.77	34.8	34.8	.0509	19.66	-1.2936	1.6070	+
3667	"	11/11/76	45.50	258.1	1.37	.57	.02	1.35	33.3	33.3	.0405	24.67	-1.3921	1.5351	+
3668	"	12/11/76	34.10	241.0	1.46	18.2	.62	.84	35.4	35.4	.0237	42.14	-1.6247	1.6775	+
3669	"	18/11/76	4.66	149.2	1.16	25.1	.86	.30	45.1	45.1	.0067	150.33	-2.1771	2.5655	+
3670	"	19/11/76	6.52	162.1	3.97	97	3.3	.67	41.1	41.1	.0163	61.34	-1.7878	2.4220	+
3671	"	22/11/76	9.97	179.8	.39	.72	.02	.37	39.0	39.0	.0095	105.41	-2.0229	2.2381	+
3672	11	23/11/76	13.40	193.0	.623	3.08	.1	.52	39.8	39.8	.0131	76.54	-1.8839	2.1079	+
3673	"	24/11/76	16.72	203.5	1.08	3,. 34	.11	.97	38.4	38.4	.0253	39.59	-1.5976	2.0090	+
l/5a	BR45	21/9/87	33.75	240.5	1.33		0	1.33	34.4	34.4	.0387	25.86	-1.4127	1.6825	Δ
l/5b	"	"	ii	240.5	1.32	n.d.	0	1.32	34.4	34.4	.0384	26.06	-1.4160	1.6825	Δ
1/14	"	"	3.15	135.2	.439	3.58	.128	.311	35.9	*44.8	.0069	144.05	-2.1585	2.7311	Δ
2/5a	"	23/9/87	34.50	241.8	1.23	n.d.	0	1.23	33.8	33.8	.0364	27.48	-1.4390	1.6719	Δ
2/5b	"	"	"	241.8	1.12	n.d.	0	1.12	33.8	33.8	.0331	30.18	-1.4797	1.6719	Δ
2/14	"	"	2.33	125.1	.334	4.31	.152	.182	38.3	*45.8	.0040	251.65	-2.4008	2.8580	Δ
3/5a	"	25/9/87	22.50	218.4	1.1	n.d.	0	1.10	36.7	36.7	.0300	33.36	-1.5233	1.8740	Δ
3/5b	"	"	"	218.4	1.06	n.d.	0	1.06	36.7	36.7	.0289	34.62	-1.5394	1.8740	Δ
3/14	"	"	7.40	167.2	.581	n.d.	0	.581	37.8	M1.4	.0140	71.26	-1.8528	2.3675	Δ

* Gross dilution for the water occurred I.e. 10 to 20%.

o, +, A are symbols used 1n Figure 1 and Figure 2.

concentration in the water phase (in g/tonne). The distribution coefficient (K_D) which is the ratio of the boron concentration in the steam to that in the water (in g/tonne) is shown together with $1/K_D$ and $\log K_D$. The final parameter is log (density of water/density of steam) i.e. $\log d_\ell/d_v$.

Discussion

The results are plotted in two ways (Fig. 1 and Fig. 2).

Figure 1 plots $\log K_D$ v $\log d_\ell/d_v$.

This form of graph is useful for plotting distribution coefficients as it has one fixed point through which all curves must pass i.e. at the critical point the concentrations in the steam and water are equal and the density of steam and water are equal (or steam and water are indistinguishable). Thus $K_D = 1 = d_\ell/d_v$ or $\log K_D = 0 = \log d_\ell/d_v$. The present data (from Table 1), *the* critical point data and data at 100°C and 101.6°C, from Jaulmes et al and Van Stackelburg et al. respectively, were used to calculate the best fit curve. The computer statistical analysis programme SAS was used to fit a quadratic equation. The critical point and the 100°C and 101.6°C data were weighted to ensure the curve passed through the first and close to the other points. Emphasis was placed on the latter points as they were averages of 20 and 10 determinations respectively. Present data from Table 1 was weighted in favour of steam analyses with high boron (>1 g/tonne) and against those with low boron (<1 g/tonne) and high chloride contamination. The calculated equation of the regression curve is:

$$\log K_D = -0.947 \log d_\ell/d_v + 0.0547 (\log d_\ell/d_v)^2$$

Three other curves are shown in Figure 1.

1. Styrikovich et al (1960) - equation (2)
2. Tonani (1970) - equations (3) and (4)
3. Tonani (pers. comm.) - equation (5).

Also shown are data from Byrnes (1962), and from Tskhvirashvili et al (1964). N.B. Ellis and Mahon's tabulated values for 150, 200, 250 and 300°C are not shown as they lie on Styrikovich's line.

Figure 2 shows all the data in Figure 1 plotted as $1/K_D$ versus temperature (°C). The curve has been transposed from Figure 1 in five degree intervals but no equation has been calculated. However a linear equation fits to ±3% between 150 and 320°C:

$$1/K_D = 10^{[3.0506 - 0.00669\ t]} \tag{6}$$

or

$$t°C = 456 + 149.5 \log K_D \tag{7}$$

Comparison of Previous Equations to the Experimental Data

Examination of the graphs show how well (or badly) the various suggested equations fit with the data.

The form of Tonani's equations are such that $K_D \neq 1$ at critical point and therefore are intrinsically a poor approximation at high temperatures.

Styrikovich's equation fits well with known data at high temperatures (above 300°C) but deviates as the temperature decreases.

FIG 1

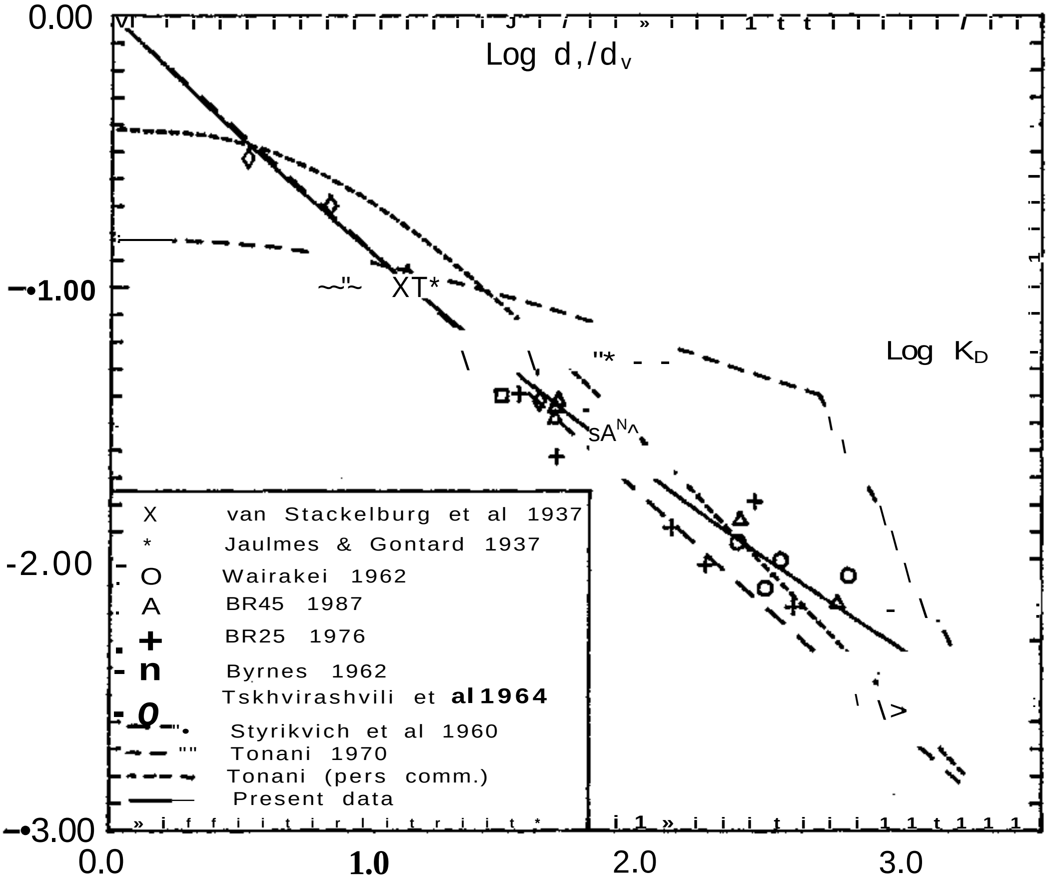
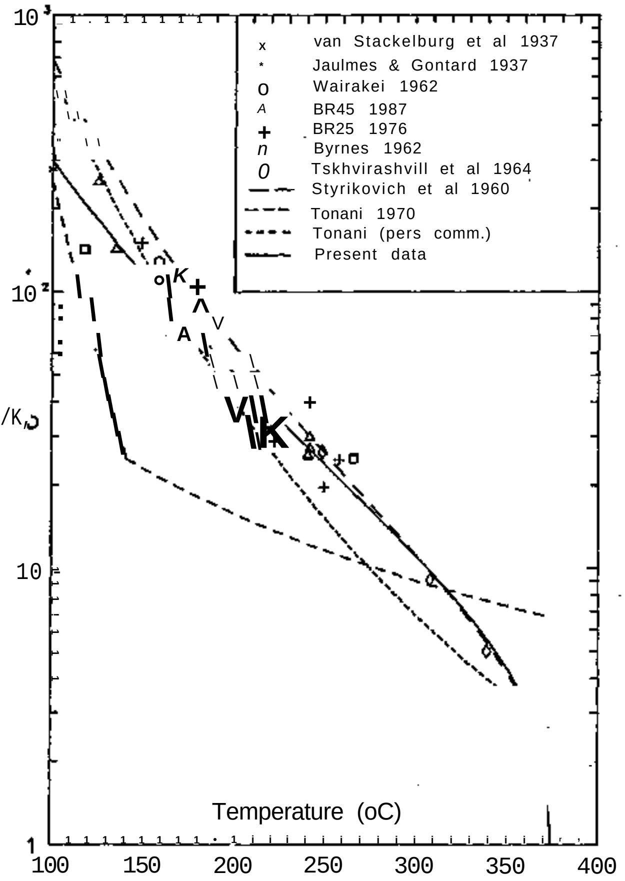


FIG 2



Application of Volatility Data to Geothermal Systems

1. Generation of boron rich shallow waters.

Tonani (1970) examined this in detail. Even with a high separation temperature of 300°C, K_D = 0.09 i.e. the concentration in the steam is less than 1/10 of that in the reservoir and total condensation of the steam at shallow level will not yield a higher concentration. However, partial condensation, especially at a lower temperature will concentrate the boron in the liquid, e.g. with condensation at 100°C of *1%* of the steam formed at 300°C the concentration in the liquid would be approximately 7 times that in the original liquid. If steam flowed through shallow surface water with steam inflow equal to evaporation, and negligible liquid outflow then very high concentrations of boron could be achieved. Tonani (1970) reports concentrations as high as 30 times the concentration in the reservoir.

Mixture of *one* of these boron rich aquifers with the deep water would reduce the Cl/B ratio in the mixed water. This could explain changes of the Cl/B ratio at Wairakei from 26 to 22.

2. Generation of boron deficient deep waters.

Steam loss can occur by adiabatic (isoenthalpic) evaporation (AE) or by isothermal evaporation (IE). In the case of adiabatic evaporation the process could be single stage *(SS)*, in which all the steam formed is in equilibrium with the residual water phase, or continuous separation (CS), in which each small amount of steam, formed in equilibrium with the water, is immediately removed from any further steam separation equilibria. In the single stage process K_D at the final separation temperature is used, while in the continuous separation process K_D starts at the initial temperature and adjusts as separation continues. As K_D is larger at high temperatures, more boron is removed by continuous separation than by single stage.

TABLE 2: Changes in Chloride and Boron concentration with evaporation.

Starting Temp °C	Process	Final Temp °C	Cl_f/Cl_i	B_f/B_i	$(Cl/B)_f/(Cl/B)_i$	Steam Fraction
350	AE/CS	100	2.192	2.069	1.059	0.544
300	AE/CS	100	1.647	1.620	1.029	0.393
350	AE/SS	100	2.245	2.233	1.005	0.555
300	AE/SS	100	1.694	1.690	1.003	0.410
350	IE/CS		2.192	1.880	1.166	0.544
300	IE/CS		1.647	1.574	1.046	0.393
350	IE/SS		2.245	1.806	1.243	0.555
300	IE/SS		1.694	1.594	1.063	0.410
350	IE/SS		6.12	3.06	2.00	0.837
350	IE/SS		12.05	6.025	2.00	0.917

AE/CS = Adiabatic evaporation + continuous steam loss
AE/SS = Adiabatic evaporation + single stage steam loss
IE/CS = Isothermal evaporation + continuous steam loss
IE/SS = Isothenral evaproation + single stage steam loss
SF = Steam fraction i.e. total steam formed/initial water
i = initial value
f = final value

N.B. All data are calculated using K_D values obtained from equation 6.

Table 2 shows the changes in chloride and boron concentrations and Cl/B ratio in the residual water as steam separation occurs. Two initial temperatures *are* used, 350°C and 300°C. For adiabatic evaporation from 350°C, the Cl/B ratio increases by 5.9%. To obtain this small increase in the Cl/B ratio the chloride concentration has more than doubled. Thus this mechanism cannot be used to explain the doubling of the Cl/B ratio in the Tongonan water where the Cl/B ratio doubles between the deep and spring waters and the chloride concentration is reduced from 8000 to 4000 g/t. Using a deep water temperature in the measured samples of approximately 300°C, the adiabatic expansion cannot explain the changes.

Isothermal evaporation at high temperature changes the Cl/B ratio much more than adiabatic evaporation for the same steam formation, i.e. at 350°C we can reach $(Cl/B)_f/(Cl/B)_i$ = 1.24 or a 24% increase. However using an initial temperature of 300°C, only a 6.3% increase is attained.

If isothermal evaporation at 350°C or 300°C doubles the initial Cl/B ratio it also raises the chloride concentration by 6.12 times or 12 times respectively. Thus even at 350°C the isothermal evaporation would have to be followed by a 12 fold dilution to attain Cl_f/Cl_i = 0.5, as occurs at Tongonan. This appears unlikely and it is therefore necessary to invoke other mechanisms besides evaporation to explain the observed data from Tongonan. Adsorption of B into illite is known to occur and is a possible mechanism (Couch and Grim, 1968; Hoashi, 1986).

CONCLUSIONS

The distribution coefficient of boron, K_D can be expressed:

$$\log K_D = -0.947 \log d_\ell/d_v + 0.0547 (\log d_\ell/d_v)^2$$

and between 150 and 320°C an approximate relationship is:

$$1/K_D = 10^{[3.0506 - 0.00669\ t]}$$

The volatility of boron in geothermal systems can explain high boron concentrations in shallow aquifers and changes from high to low Cl/B ratios in flowing systems.

However, it is more difficult to explain the generation of boron deficient solutions i.e. changes from low Cl/B ratios to high Cl/B ratios cannot be explained by volatility alone and other mechanisms such as adsorption of boron onto clays (e.g. illites) are necessary.

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