GRAPHICAL TECHNIQUES FOR THE EVALUATION OF WATER/ROCK EQUILIBRATION CONDITIONS BY USE OF NA, K, MG AND CA-CONTENTS OF DISCHARGE WATERS

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ABSTRACT

Relative Na, K, Mg, Ca-contents of thermal waters, in full equilibrium with a thermo-dynamically stable mineral system, are, at a given temperature, uniquely fixed. They provide useful reference values for the assessment of the degree of attainment of fluid-rock equilibrium in natural systems. The solute pair Na-K equilibrates most slowly or only at elevated temperatures, while relative K-Mg-contents adjust much faster and at low temperatures. The system K-Ca is sensitive to variations in P_{CO_2}. These sub-systems are combined in graphical techniques for the evaluation of deep temperature and P_{CO_2}-conditions in geothermal systems on the basis of the Na. K, Mg and Ca contents of their discharges.

INTRODUCTION

Most of the ionic solute geothermometers presently in use, such as those based on the sodium-potassium contents of thermal waters (White, 1965: Ellis and Mahon, 1967; Arnorsson et al., 1983). on sodium-lithium contents (Fouillac and Michard, 1981) or sodium-potassium-calcium contents (Fournier and Truesdell, 1973) have been calibrated empirically. This, ana the lack of a sound theoretical basis in the derivation of e.g, the latter two, render interpretation of deviations from the expected behaviour difficult. By devising procedures based largely on theoretical considerations, a wide range of processes affecting a geothermal solution during its rise to the surface may be taken into account: by employing a graphical technique the effects of a variety of processes may be assessed simultaneously for a large number of samples.

CONCEPTUAL FRAMEWORK

Based on an earlier investigation into mass transfer processes in hydrothermal systems (Giggenbach, 1984). the predominant rock alteration process accompanying the rise of thermal waters is potassium metasomatism which in turn means that of the four cations, Na. K, Mg. Ca. potassium is removed from the liquid phase to be taken up in potassic alteration products, Na, Mg, Ca are added to the solution through dissolution of corresponding minerals. Attainment of water-rock equilibrium depends to some degree on the kinetics of individual mineral dissolution and deposition reactions, but may to a first approximation be discussed in terms of the overall rate of rock alteration, the process governing the release and uptake of fluid phase components.

With the amount of rock to be altered being proportional to the amount of solute to be added or removed from solution, it is much "easier" for a minor solution component present in "ppm" amounts to readjust to changes in its physical or chemical environment than'for one present in concentrations several thousand times higher. Everything else being equal, reactions involving the minor constituents of a geothermal water, Mg and Ca, then can be expected to respond much faster than those involving the generally predominant cationic species, Na. with K occupying an intermediate position. As the speed of rock alteration is also a function of temperature, Mg- and Ca-contents of thermal waters can be expected to equilibrate with the mineral system quite rapidly even at low temperatures, sodium only slowly and at high temperatures, with potassium bridging both systems.

In dynamic, such as geothermal systems, overall fluid-rock equilibrium is rarely attained (Giggenbach, 1981) and the fluids sampled are likely to have reached some complex steady state composition reflecting the combined effects of initial fluid composition, the kinetics of primary mineral dissolution and secondary mineral deposition at decreasing temperatures and pressure, in addition to vapor loss, dilution and mixing with fluids of different origin. In the midst of all these complexities, the state of equilibration, termed "full equilibrium" (Giggenbach, 1984) provides a useful reference system for the discussion of actual fluid and mineral compositions. It corresponds to complete isochemical recrystallisation of the primary rock matrix to an alteration assemblage thermodynamically stable at a given temperature and pressure, a state possibly attained only in a stagnant system of infinite age.
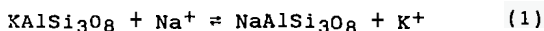
In contrast to the steady state composition, the mineralogical composition of the full equilibrium system is accessible to rigorous evaluation and corresponds for average intermediate to acid crustal rocks to an assemblage containing sodium in the form of albite, Mg as chlorite, Ca as epidote or a zeolite (laumontite at low, Wairakite at high temperatures, with the pair K-feldspar/ K-mica providing the buffer to accommodate the aluminium not used up in the formation of the Na, Mg, Ca-minerals. Relative Na, K, Mg and Ca-contents of a water coexisting with this full equilibrium assemblage at a given temperature are uniquely fixed and may be used as reference points for comparison with actually observed compositions.
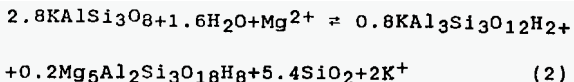
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In the application of these findings to a wide range of geothermal discharges (Giggenbach, unpublished results; Giggenbach et al., 1983), the two sub-systems Na, K, Mg and K, Mg, Ca were found to be especially useful in the evaluation of physical and chemical conditions within geothermal systems. The components of the first sub-system are likely to be controlled essentially by temperature dependent interactions of the waters with aluminium-silicates, their relative concentration can therefore be expected to provide indicators for water-rock equilibration temperatures. The involvement of Ca in the formation of calcite, an ubiquitous constituent of hydrothermal alteration assemblages, renders the second sub-system a suitable candidate for the formulation of a geo-indicator sensitive to the effects of the most important component of the vapor phase: carbon dioxide.

THE SYSTEM NA. K, MG

Accepting the full-equilibrium assemblage resulting from the iso-chemical recrystallisation of an average crustal rock at geothermally relevant temperatures (100°- 300°C) to contain Na in the form of albite, Mg as chlorite, and potassium in the form of feldspar and a layer silicate, the reactions governing the chemistry of any coexisting solution, in terms of idealised endmember minerals, are:

$$KAlSi_3O_8 + Na^+ \rightleftharpoons NaAlSi_3O_8 + K^+ \quad (1)$$

and

$$2.8KAlSi_3O_8 + 1.6H_2O + Mg^{2+} \rightleftharpoons 0.8KAl_3Si_3O_{12}H_2 +$$

$$+0.2Mg_5Al_2Si_3O_{18}H_8 + 5.4SiO_2 + 2K^+ \quad (2)$$

Their corresponding equilibrium constants are

$$K_1 = (a_{K^+}/a_{Na^+})(a_{albite}/a_{microcline}) \quad (3)$$

$$K_2 = (a_{K^+}^2/a_{Mg^{2+}}) * (a_{muscovite}^{0.8} *$$

$$*a_{clinochlore}^{0.2} a_{silica}^{5.4}/a_{microcline}^{2.8}) \quad (4)$$

where a_i are the activity of the solute species i on the molal scale, and a_k the activity of the endmember component k in natural feldspar, illite or chlorite solid solutions.

Conversion of solute activities a_i to the commonly used concentration scale, c_i (mg/kg), is carried out by use of

$$a_i = c_i \gamma_i/1000 A_i \quad (5)$$

where γ_i is the total or stoichiometric ion activity coefficient of the species i and A_i its atomic weight. For the iso-coulombic reactions considered here, the activity coefficients for mono- and divalent ions can be assumed to be closely related through $\gamma_1^2 = \gamma_2$ (Lindsay, 1980) and the above activity quotients become

$$a_{K^+}/a_{Na^+} = 0.59 \ c_{K^+}/c_{Na^+} \quad (6)$$

and

$$a_{K^+}^2/a_{Mg^{2+}} = c_{K^+}^2/62914 c_{Mg^{2+}} \quad (7)$$

The albite/microcline activity ratio of eqn(3) may safely be assumed to be close to unity. In the case of the muscovite-clinochlore-silica/microcline activity quotient, the activity of silica in solution was assumed to be that of chalcedony, the incorporation of muscovite and clinochlore into natural illites and chlorites and the corresponding reduction in their activities was taken into account by assigning a value of 0.3 to the $a_{muscovite}^{0.8} a_{clinochlore}^{0.2}$-product.

This correction is somewhat arbitrary but agrees well with observations on a wide range of geothermal waters (Giggenbach, unpublished results). The simplifications made in the present approach, however, should be kept in mind when comparing theoretical and analytical water compositions.

One way to carry out such comparison is based on the evaluation of apparent temperatures of equilibration for a given reaction. The temperature dependence of the Na/K-ratio is that obtained on a wide range of deep drill-hole discharges with known bottom hole temperatures (Giggenbach, unpublished results), that for the K^2/Mg-quotient by use of thermodynamic data provided by Helgeson et al. (1978) and the above activity correction. They are

$$L_1 = L_{kn} = \log(c_{K^+}/c_{Na^+}) = 1.75-(1390/T) \quad (8)$$

and

$$L_2 = L_{km} = \log(c_{K^+}^2/c_{Mg^{2+}}) = 13.95-(4410/T) \quad (9)$$

for which potassium-sodium temperatures, t_{kn}, and potassium-magnesium temperatures, t_{km} (°C), may be obtained according to

$$t_{kn} = (1390/(1.75-L_{kn}))-273.2 \quad (10)$$

$$t_{km} = (4410/(13.95 - L_{km}))-273.2 \quad (11)$$

As pointed out above, the overall rate of water-rock interaction can be expected to decrease rapidly with decreasing temperature which in turn leads to a rapid decrease in the absolute amounts of solution components able to be exchanged with the rock matrix (Giggenbach, 1984). Maintenance of water-rock equilibrium for reactions involving major solutions components (Na,K), therefore, is likely to be impaired at an earlier stage or at higher temperatures as compared to a reaction involving the minor components K, Mg. Evaluation of equilibration temperatures by use of the above two geothermometers (eqns (10) and (11)), therefore, is bound to lead to differing results. The confusion is increased by deriving a third geothermometer, through a linear combination of eqns (8) and (9) according to

$$L_{nm} = \log(c_{Na^+}^2/c_{Mg^{2+}}) = L_{km}-2L_{kn} =$$

$$= 10.45-1630/T \quad (12)$$

Each of the above geothermometers is equally valid in a system in full equilibrium. Taking into account the kinetics of rock alteration, however, the range of applicability of eqn(11) is likely to extend to much lower temperatures than that of eqn(10). In the case of L_{nm}, the general absence of Na-minerals in typical lower temperature, hydrothermal alteration assemblages (Browne, 1978) suggests that reactions such as

$$Na-Al-silicate + Mg^{2+} \rightleftharpoons chlorite + 2Na^+ \quad (13)$$
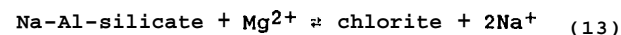
are not important in controlling relative Na-Mg-contents, except in high temperature systems.

Because of the dependence of rock alteration rates on a wide range of parameters, such as fluid flow rates, effective surface areas, dissolution and deposition rates of individual minerals, in addition to temperature, it is impossible to assign definite validity ranges to either the Na-K-or the K-Mg-geothermometer. Rather than splitting the system Na,K, Mg into two sub-systems, Na-K, and K-Mg, it appears more advantageous to base initial evaluation of deep equilibration conditions on a technique allowing assessment for all three components and preferably for a wide range of samples simultaneously.

The graphical technique well suited to the evaluation of relationships among three variables is based on the use of tri-linear or triangular diagrams. Because of the presence of the non-linear term a_{K+}^2 in eqn (4). the position of theoretical and analytical data points, however, remains a function of absolute solute contents. This problem is overcome by plotting such data in terms of relative values of Na^2, K^2, Mg or Na, K, $\sqrt{Mg}$, the latter conducive to a less "spread-out" presentation (Fig. 1). In gaining the ability to represent data for solutions of any salinity in one diagram, one of the best features of tri-linear plots, the straight-line representation of mixing relationships, had to be sacrificed. For processes essentially consisting of variations in the relative contents of magnesium, the one "odd man out", mixing lines still remain straight.

In order to facilitate practical applications solute contents in mg/kg are used, in order to accommodate most geothermal waters, sodium contents have to be divided by 1000, potassium by 100 and the square root is taken of magnesium contents as measured. The Na-K- and K-Mg-geothermometers are represented by two sets of isotherms. Their intersections correspond to the composition of waters in equilibrium with both sets of mineral systems, the resulting curve is marked "full equilibrium" in Fig. 1.

Application of the technique to geothermal systems is illustrated by use of analytical data for a number of closely related natural and deep well discharges listed by Iienley et al. (1984). The well discharges plot all very close to the full equilibrium line at temperatures very close to those measured, corresponding spring discharges are shifted to lower temperatures and to positions off the full equilibrium line. For the very high temperature systems Tongonan and Cerro Prieto, the position of the corresponding spring waters corresponds to a Na/K-equilibration temperature t_{kn} of 250°, at a t_{km} of 225° indicating some considerable re-equilibration of the waters during their rise from drilled depth to the surface. For Broadlands and Wairakei pool discharges, t_{kn} is 225° with t_{km} for Wairakei being with 185° considerably below that of around 210' for Ohaki Pool. The differences in t_{km} are likely to reflect differences in the rise velocities of the waters, those having supplied the Champagne Pool at Wairakei likely to have ascended more slowly thus allowing K-Mg to adjust to lower temperature conditions. This effect is even more pronounced for Ngawha where t_{km} for Jubilee Bath, an almost stagnant pool, is with 145' well below that of the deep water of 220°.

By plotting a series of natural spring discharges, a pattern corresponding to a "cooling curve" of waters within a system is likely to emerge which then may be extrapolated to the full equilibrium line to obtain actual deep water-rock equilibration temperatures. The procedure is not very sensitive to the effects of steam loss or dilution. Lines allowing the effects of these two processes to be assessed are shown in Fig. 3.

Fig.   ~ Relative Na. K. Mg-contents of geothermal waters. Cvaluation of water rock-equilibration temperatures.
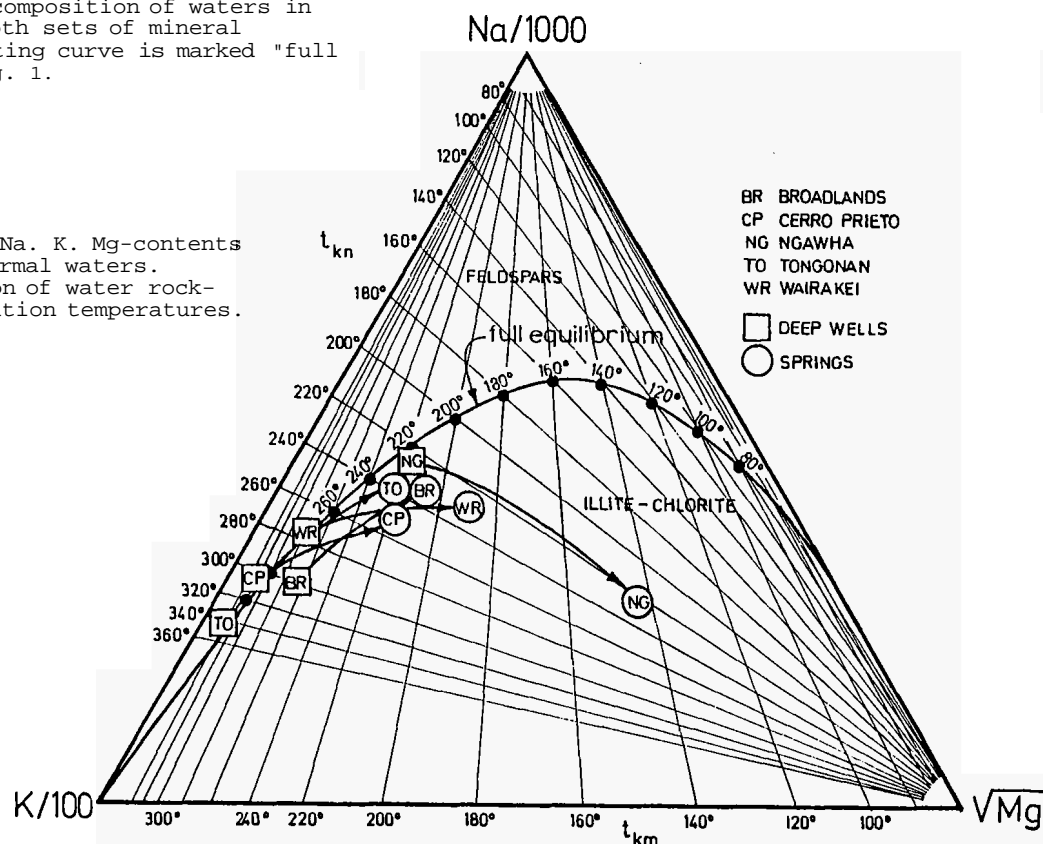
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The diagram is especially sensitive to the admixture of low temperature, high magnesium, usually bicarbonate waters. Data points for such waters, of doubtful value in the determination of deep equilibration conditions, plot close to the far-from-equilibrium Mg-corner. The diagram therefore is self-policing allowing immediate assessment of the reliability of a water sample for the evaluation of deeper temperatures, the larger the distance of a data point from the full equilibrium line, the lower the reliability of the Na/K-temperatures indicated. K-Mg-temperatures, however, may still be obtained as an estimate of water-rock equilibration temperatures at shallow levels. The technique should only be applied were equilibration with an illite-chlorite containing mineral phase can be assumed, a condition generally fulfilled in the case of near neutral chloride-bicarbonate waters, but not in the case of acid sulfate, or chloride-sulfate waters. The same limitations apply to the other subsystem, K, Mg, Ca.

THE SYSTEM K, MG, CA

The Na-K-Ca-geothermometer as derived by Pournier and Truesdell (1973) is essentially a $\sqrt{Ca}/K$-geothermometer, its apparent success is based on the quite pronounced temperature dependence of this quotient. As already pointed out quite early by Paces (1975), the geothermometer is also sensitive to variations in P_{CO_2}, a finding not too surprising taking into account the fact that calcium is a constituent of calcite, an ubiquitous CO_2-containing mineral in hydrothermal alteration systems. Well before the arrival of the Na-K-Ca geothermometer, Ellis (1970) had already pointed out the sensitivity of the system Na-Ca to P_{CO_2} and had proposed a technique for the evaluation of deep CO_2 partial pressures by use of Na-Ca-contents of thermal waters.

In a full equilibrium system, f_{CO_2}, the fugacity (or partial pressure) of CO_2, again is, at a given temperature, uniquely fixed according to the univariant reaction

$$\text{Ca-AI-silicate} + \text{K-feldspar} + CO_2 = \text{calcite} + \text{illite} + \text{quartz} \quad (14)$$
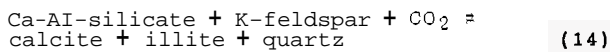
where the Ca-Al-silicate is the thermodynamically stable Ca-mineral of the isochemically recrystallised, full equilibrium assemblage as described above. The temperature dependence of this reaction is adequately given by (Giggenbach, 1984)

$$\log f_{CO_2} \approx \log P_{CO_2} = 0.0168t - 3.78 \quad (15)$$

As pointed out above, equilibration of fluid phase components with the rock matrix is much "easier" for minor components. CO_2 generally being a major component, most geothermal fluids are likely to contain CO_2 in non-equilibrium amounts, still allowing the minor constituents, K, Mg, Ca, to adjust to the prevailing temperature and f_{CO_2}-conditions. The approach to full equilibrium then may be described in terms of a reaction consisting of the deposition of calcite and conversion of feldspar to layer silicates, again in terms of idealised endmembers, according to

$$3 \; KAlSi_3O_8 + CO_2 + Ca^{2+} = \\ KAl_3Si_3O_{12}H_2 + CaCO_3 + 6SiO_2 + 2K^+ \quad (16)$$
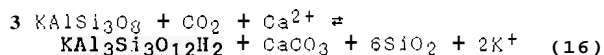
Its equilibrium constant, K_{16}, corresponds to

$$K_{16} = (a^2_{K^+}/a_{Ca^{2+}}f_{CO_2})^* \\ *(a_{musc.}a^6_{calcite}a_{silica}/a^3_{microcline})(17)$$

Again the assumption $\dot{\gamma}^2_1 = \dot{\gamma}_2$ is made, the silica activity is assumed to be that of chalcedony, and $(a_{muscovite}a_{calcite}/a^3_{microcline})$ is set to unity. Under these circumstances the values of $L_{16} = \log K_{16}$ as calculated by data given by Helgeson et al. (1978) are with 1.66 ± 0.14 from 50' to 300' almost temperature independent. Together with the conversion factor from activities to mg/kg, the relationship linking $c^2_{K^+}/c_{Ca^{2+}}$ to P_{CO_2} is with adequate accuracy given by

$$L_{kc} = \log(c^2_{K^+}/c_{Ca^{2+}}) = \log P_{CO_2} + 3.0 \quad (18)$$

Nothwithstanding the temperature independence of L_{16}, CO_2- partial pressures in geothermal systems are strongly dependent on temperature. In order to be able to correlate the CO_2-partial pressures found by use of eqn(18) with their corresponding equilibration temperatures, a geothermometer equilibrating with similar speed and under similar conditions as the K-Ca-geobarometer is required. The nearest such system is that based on potassium-magnesium as described above. The overall system used again involves three solution components and therefore would be suitable for evaluation by use of trilinear diagrams. Because of the intricate correlations among P_{CO_2} and the CO_2-contents of coexisting liquid and vapor phases, a more open presentation as shown in Fig. 2 is preferred.

There values of L_{kc} are plotted versus L_{km}. Again a line representing CO_2-partial pressures for a full equilibrium assemblage as given by eqn(15) is shown. Data points below this line correspond to the composition of "immature" fluids containing higher than full equilibrium CO_2-contents and therefore being still reactive with respect to hydrogen metasomatism. Values above the full equilibrium line may be the result of isothermal boiling or dilution. The latter processes is likely to be responsible for the position of deep well data points at lower than equilibrium CO_2-partial pressures for Wairakei, Cerro Prieto and Tongonan. The process is thought to consist of the dilution of a deeper full equilibrium, high CO_2 brine by conductively or steam heated groundwaters giving rise to the formation of the lower CO_2 fluids produced from the wells. A more detailed evaluation of relationships in Fig. 2 is possible by use of similar P_{CO_2} versus temperature diagrams presented earlier (Giggenbach, 1984) Also detailed correlation of K-Ca-CO_2-partial pressures with observed gas-contents is beyond the scope of this introduction. Support of the general validity of the approach is provided by the position of data points for Wairakei and Rroadlands, the latter being roughly ten times as "gassy" as the former. The convergence of data points for spring discharges onto the K-feldspar/illite-line suggests continuing re-equilibration and close attainment of full equilibrium of the waters at an effective temperature of around 200°C. The set of analytical data provided by Henley et al. (1984) is not necessarily representative of all discharges of a given field and considerable deviations from the patterns shown in Fig. 2 may result by use of other data.
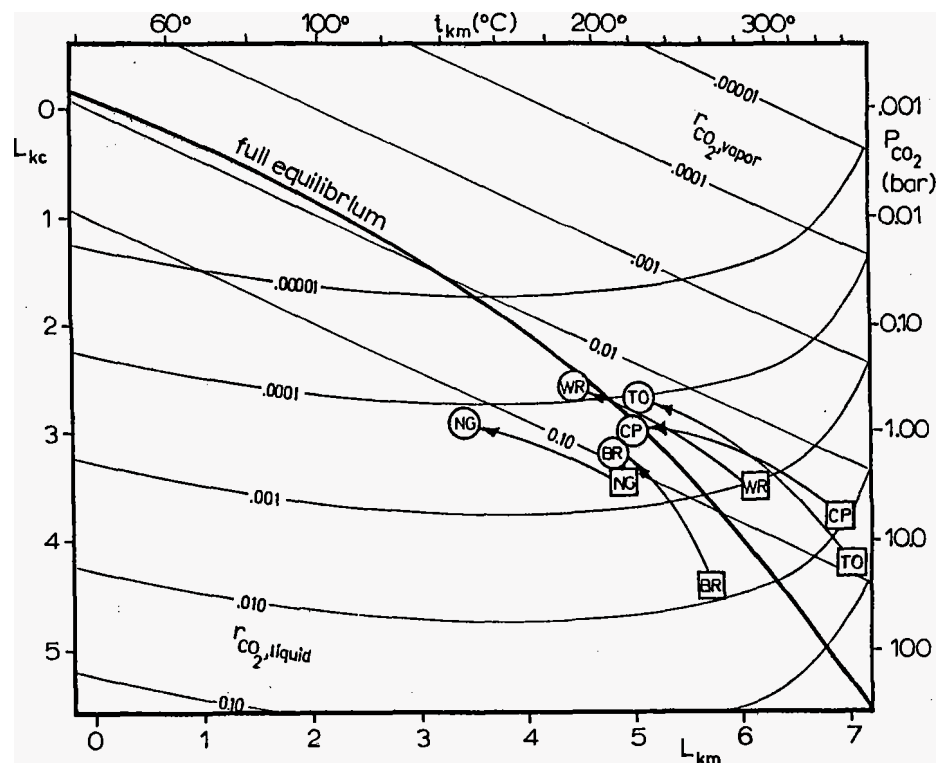
Fig. 2 -

Evaluation of CO_2-partial pressures in geothermal systems by use of K, Mg, Ca-contents of their discharges ; for symbols see Figure 1.

PRACTICAL APPLICATION

The technique proposed here for the evaluation of deep fluid-rock equilibrium conditions is best carried out by use of the two diagrams shown. In order to facilitate application, simplified versions are given below, they may be photocopied or may be re-created by use o data usea in their construction given in Table 1.

TABLE 1

Data useful in the construction of Figs 3 and 4. Number of eqn used, in brackets.

t (°C)	$\frac{Na}{1000}$	$\frac{K}{100}$	$\sqrt{Mg}$	P_{H_2O} (b)	B_{CO_2}	P_{CO_2} (b)
	(8)		(9)	(20)	(22)	(15)
40	48.80	1.0	116.00	0.09	21000	.0008
60	26.40	1.0	44.00	0.23	12710	.0017
80	15.30	1.0	18.50	0.51	7690	.0037
100	9.40	1.0	8.60	1.05	4650	.0079
120	6.10	1.0	4.30	2.00	2010	.0172
140	4.10	1.0	2.30	3.58	1700	.0373
160	2.88	1.0	1.30	6.06	1030	.0810
180	2.08	1.0	0.78	9.80	620	,1750
200	1.54	1.0	0.48	15.20	375	0.38
220	1.17	1.0	0.31	22.80	227	0.82
240	0.91	1.0	0.21	33.10	138	1.79
260	0.72	1.0	0.15	46.70	83	3.87
280	0.58	1.0	0.10	64.30	50	8.39
300	0.47	1.0	0.07	86.50	30	18.20
320	0.39	1.0	0.06	114.20	18	39.50
340	0.33	1.0	0.04	148.00	10	85.50

In the presentation of the system Na, K, Mg of Fig. 3, two areas are distinguished. One adjoining the full-equilibrium line and marked "partial equilibrium, dilution or mixing" contains Na-K-isotherms, there t_{kn} may still be relevant and may reflect deeper, effective Na-K-equilibration conditions. The area near the Mg-corner marked "shallow waters" contains K-Mg-isotherms, there t_{kn} is unlikely to reflect fluid-rock equilibrium and only t_{km} should be used as a measure for fluid-rock equilibration temperatures, albeit at shallow levels. Both diagrams should only be applied to near neutral chloride-bicarbonate waters.

The isotherms of Fig.[1] are readily obtained by use of values for Na/1000 and $\sqrt{Mg}$ normalised to K/100 as shown in Table 1. The CO_2-contents in coexisting liquid and vapor phases as a function of P_{CO_2} in terms of r_{CO_2}, the molar ratio of CO_2 to water, were obtained according to

$$P_{CO_2} = r_{CO_2,vapor} P_{H_2O} = r_{CO_2,liquid} B_{CO_2} P_{H_2O} \quad (19)$$

where P_{H_2O} is the vapor pressure of water varying with temperature t (°C) according to

$$logP_{H_2O} = 5.51 - 2048/(t+273.2) \quad (20)$$

and B_{CO_2} is the vapor/liquid distribution coefficient for CO_2

$$B_{CO_2} = r_{CO_2,vapor}/r_{CO_2,liquid} \quad (21)$$

Its temperature dependence (Giggenbach, 1980) is given by

$$logB_{CO_2} = 4.7593-.01092t \quad (22)$$

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Over the temperature and pressure ranges covered by Figs 2 and 4, both H_2O and CO_2 are assumed to behave ideally. The CO_2^- content of the fluids in weight-% may he obtained from the r_{CO_2}-values by use of

$$\% \ CO_2 \ b.w = 2.44 \ r_{CO_2}/(1+2.44 \ r_{CO_2}) \quad (23)$$

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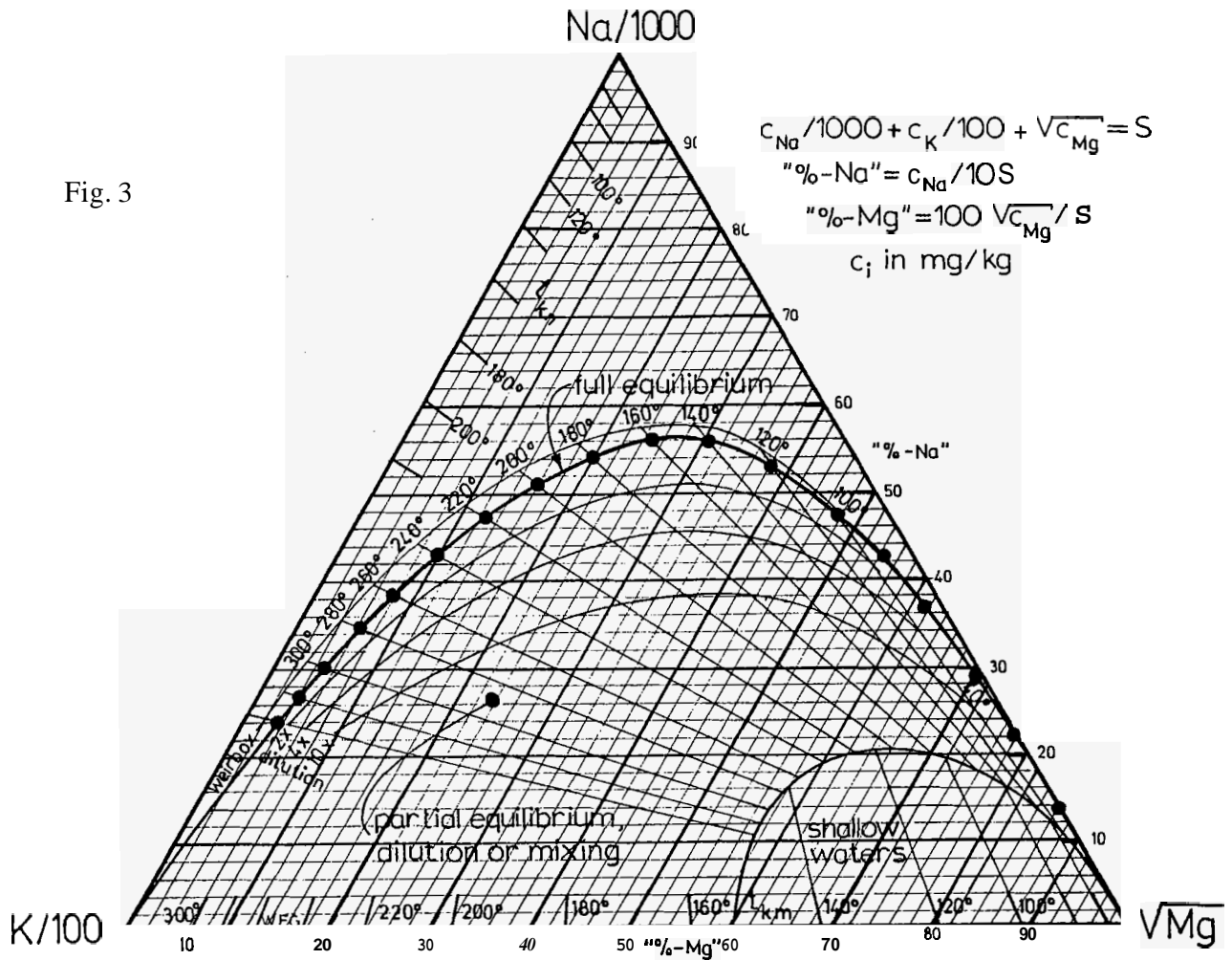
Fig. 3

$$c_{Na}/1000 + c_K/100 + \sqrt{c_{Mg}} = S$$
$$"\%-Na" = c_{Na}/10S$$
$$"\%-Mg" = 100\sqrt{c_{Mg}}/S$$
$$c_i \text{ in mg/kg}$$

Fig. *4*

$$L_{kc} = \log(c_K^2/c_{Ca})$$
$$r_{co_2} = n_{co_2}/n_{H_2O} = x_{co_2}/x_{H_2O}$$
$$L_{km} = \log(c_K^2/c_{Mg})$$