# MIXING TRENDS AND SOLUTE GEOTHERMOMETRY OF BOREHOLE WATERS FROM THE PAKA GEOTHERMAL PROSPECT, KENYA.

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## ABSTRACT

Borehole water in the Paka Geothermal prospect are predominantly mixed sodium bicarbonate- chloride water type with low chloride concentrations.(28-161 ppm) and could be influenced more by evaporite processes and leaching of solutes . The pH of the water from the boreholes range between (6.7and 8.5). Temperatures of the borehole waters were above ambient. Mixing trends determined from plots of chloride, boron, magnesium, sulphate, and enthalpy suggest there could have been boiling prior to mixing, oxidation processes by atmospheric oxygen in the shallower depths of the geothermal system as the hotter geothermal waters ascend to the surface. This was indicated by increase in sulphate concentrations. Boiling and mixing processes from chloride-enthalpy plot suggest waters were being diluted from the western to the eastern side of the prospect. Solute geothermometry temperatures of NaK and Na-K-Ca are relatively high and probably overestimates the actual temperatures of the geothermal system. Quartz temperatures were very low. Assumptions made for the applications of the solute geothermometry temperatures may not be valid due to high discrepancy between the NaK, Na-K-Ca and quartz temperatures.

## 1.0 INTRODUCTION

The Paka geothermal prospect is located within the Gregory Rift of the East African Rift valley that extends from the Afar triple junction in the Red Sea to Mozambique, Figure 1.

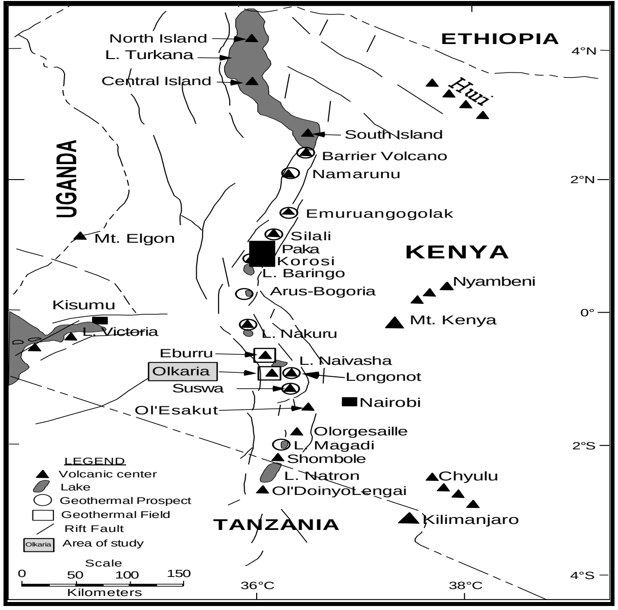

**Figure 1**: Map of the Kenya rift showing the location of Paka geothermal field and other Quaternary volcanoes along the rift axis.

It is a well defined volcano situated 25km north of Lake Baringo and 15 km east of Nginyang. It rises 600-700 m above the rift floor to reach a maximum altitude of 1697m and in plan view has an irregular outline covering an area of ~ 280 $km^2$ . The study area was within Baringo District, Rift valley Province in the Republic of Kenya. Paka Volcano lies between Korosi and Silali Volcanic centres. Paka is a small shield volcano constructed largely of trachyte lavas and pyroclastic deposits. Basalt, hawaiite and mugearite lavas were erupted from a series of fissure and fault zones located on the north east and the southern flanks. Trachyte lavas were erupted from numerous domes and cones located along N-trending and NNE-trending fissures on the upper flanks and the summit area. Further faulting and fracturing across the shield led to the formation of an axial rift zone defined by two important faults, the Eastern and Western boundary faults.

Few surface manifestations occur in the Paka geothermal prospect making the use of classical geochemical exploration techniques difficult. Boreholes are sparse and few in this prospect. However, geothermal activity manifested in the form of hot ground, steaming ground and fumaroles associated with hydrothermal alteration, is widely developed on Paka within the summit craters and upon the northern flanks. Geothermal activity on Paka is dispersed over a broad NNE-trending zone covering an area of ~ 32 $km^2$ extending from high on the southern flanks northwards across the summit area and down the northern flanks.

## 1.3 Previous work

Previous work on the geochemical aspects of the geothermal prospects to the north of Lake Baringo upto Lake Turkana was conducted by the British Geological Survey (BGS) under the auspices of the Overseas Development Administration (ODA) of the British Government and the Ministry of Energy of the Government of Kenya in the year 1985 through 1990. The initial project was to undertake preliminary geothermal reconnaissance studies of the northern part of the Rift, between Lake Baringo and Emuruangogolak volcano, with particular emphasis on several volcanic centres (Allen and Darling, 1992). Paka geothermal prospect was included in this work.

From their findings, the chemistry of fluids discharged by wells in the Paka geothermal prospect and around Paka was influenced by surface waters from rivers and streams. The ground and surface water around Paka were considered to have fluid composition of the sodium- bicarbonate type. This could have resulted from evaporite deposits as it does for example in Lake Magadi in the southern Rift. The source of the high bicarbonate water may not necessarily be from high temperature geothermal activity. Evidence of thermal water from boreholes which could indicate some outflow from a high temperature system was scant.

## 2.0 GEOLOGICAL SETTING

Paka is composed of trachyitic and basaltic lavas and pyroclastic deposits. The geological history of Paka can be broadly separated into two periods of trachytic volcanism separated by basaltic activity and faulting. Older shield-forming lavas are mantled by trachytic pyroclastic deposits which cover much of the northern, western and southern flanks of the volcano. The summit and flanks of Paka are characterised by short trachytic flows that can be discerned beneath the mantle of pyroclastic deposits. Basalt features were erupted from fissures and cones located along N-trending fractures on the northern and southern flanks, and normal faulting led to the formation of a N-trending linear zone of rifting which extends down the northern flanks. Paka is surrounded by a number of smaller satellite volcanic centres, which are linked to the main volcano by linear zones of basalt and trachyte cones and eruptive fissures. Trachytic lavas of uncertain source are overlain by younger basalt flows erupted from N-trending fissures zones extending between Paka and Korosi. The tectonic of Paka are dominated by a zone of intense normal faulting and fissuring located on the eastern and north-eastern flanks. This faulting has downfaulted older Pleistocene and Pliocene strata of the rift margin against the younger lavas of Paka, and forms part of a larger belt of deformation which extends northwards onto Silali and southwards to Korosi.

## 3.1 Boreholes sampling and analysis

The Paka geothermal prospect has a paucity of boreholes and almost non existent hot springs. The number of boreholes that could be sampled were very few. Some boreholes were drilled in the northern part of the prospect, and were abandoned. The location of most of the boreholes are shown in Figure 2.

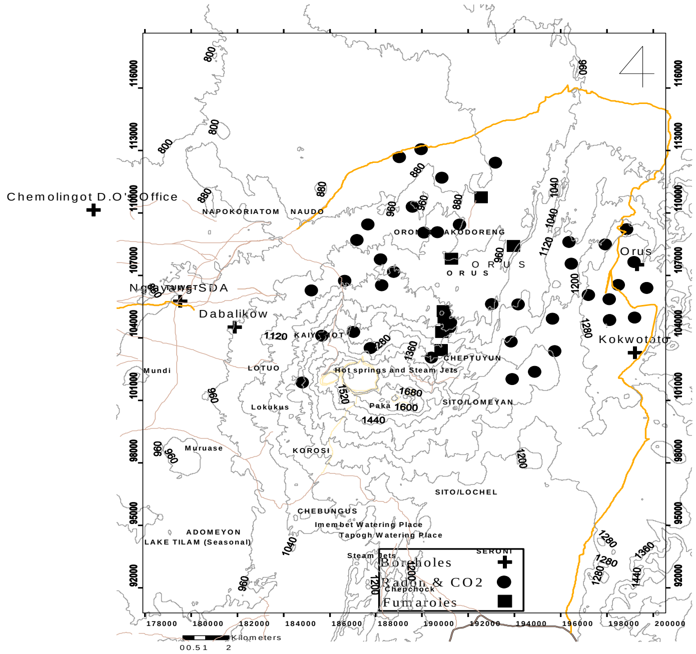

Figure 2; Location of sampled boreholes, fumaroles, radon and $CO_2$ in the Paka geothermal prospect.

The boreholes sampled were flowing boreholes. This implies that the boreholes, were mostly fitted with manual pumps and once the pump was driven manually water could be collected at the surface. Very few boreholes were driven by electric pumps e.g the ones in Orus and Kokwototo.

Sampling was done by use of a clean jug that was used to scoop the water. The jug was severally rinsed with de-ionised water before sampling. The sample was drawn while the wells flowed and was divided into several portions after filtration. The water was divided into five portions as described below and immediate analysis done.

The first portion was for immediate analysis for hydrogen sulphide ($H_2S$), carbon dioxide ($CO_2$), pH, Conductivity, and total dissolved solids (TDS). A measured amount of 5% zinc acetate solution was added to another portion of the sample for the preservation of sulphates. To samples for metal and silica analysis 1 ml of concentrated nitric acid was added for preservation. The last portion of samples was not treated in anyway. It was reserved for the analysis of chloride, fluoride, and boron. Hydrogen sulphide was analysed at the sampling site, while carbon dioxide, conductivity, total dissolved solids and pH were done at the end of each sampling day in the field laboratory. Analysis of hydrogen sulphide was done by use of the mercuric acetate technique while total carbonate carbon was determined by titrating with 0.05N HCl. Both hydrogen sulphide and carbon dioxide were analysed by titration methods using 0.001 M mercuric acetate and 0.05M hydrochloric acid respectively. Conductivity and TDS were measured using conductivity and TDS meters respectively. The measurement of pH was done by use of a pH meter. Chloride and fluoride were determined using the Mohr titration and ion selective electrode methods respectively. Silica, boron and sulphate concentrations were determined by use of UV spectrometer at wavelengths of 410, 425 and 540 nm respectively. Metal analysis was determined by use of Atomic Absorption Spectrophotometer (AAS).

## 4.0 ANALYTICAL RESULTS

### 4.1 Boreholes chemistry

The chemical composition of analysis of the water samples from the Paka geothermal boreholes is tabulated in Table 1, below.

Table 1: Chemical composition of borehole water in the Paka geothermal prospect

| Site | Temp ˚ C | pH | $H_2S$ | $CO_2$ | B | Na | K | Ca | Mg | Li | Fe | $SiO_2$ | $SO_4$ | Cl | F |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Nginyang SDA | 39 | 7.3 | 0 | 146.67 | 0.10 | 33.2 | 11.09 | 1.59 | 2.11 | 0 | 9.7 | 81.8 | 18.3 | 66 | 0.9 |
| Orus | 38 | 6.7 | 0 | 242.00 | 0.20 | 141 | 9.094 | 30.8 | 7.76 | 0 | 0.9 | 29.6 | N.D | 161 | 1.4 |
| Dabalikow | 35 | 7.1 | 0 | 251.57 | 0.30 | 93.1 | 13.35 | 5.31 | 0.65 | 0.01 | 0 | 49.2 | 18.3 | 94 | 3.8 |
| Kokwototo | 31 | 7.6 | 0 | 408.85 | 0.25 | 71.4 | 12.5 | 8.16 | 10.6 | 0 |  | 44.2 | 4.05 | 28 | 1.1 |
| Chemolingot D.O's Office | 35 | 8.5 | 0 | 303.60 | 0.15 | 13.1 | 4.363 | 2.61 | 1.08 | 0.01 | 0 | 44.8 | 23.8 | 97 | 3.7 |

The boreholes can be divided into two groups; those that fall on the Eastern part and those that fall on the Western part of the Paka volcano. The temperature of water discharged by the boreholes varied between 31 ° C for Kokwototo to 39 ° C at the Nginyang' SDA borehole. These temperatures are above ambient and also may suggest thermal input into the well fluids. The pH of the borehole water varied between 6.7 and 8.5. The Orus borehole depicts a pH of 6.7 which is slightly lower than that of neutral pH of 7. This could suggest some acidic component influence. The silica content of the Nginyang' SDA borehole was high ~ 82 ppm at measured temperatures of ~ 39 ˚ C. This could probably be associated with alkali pH which could influence the concentration of undissociated silica in water. The borehole waters were plotted on the chloride-bicarbonate-sulphate (Cl-$HCO_3$-$SO_4$) ternary diagram, Figure 3. All the borehole waters in this area plot around the bicarbonate apex.

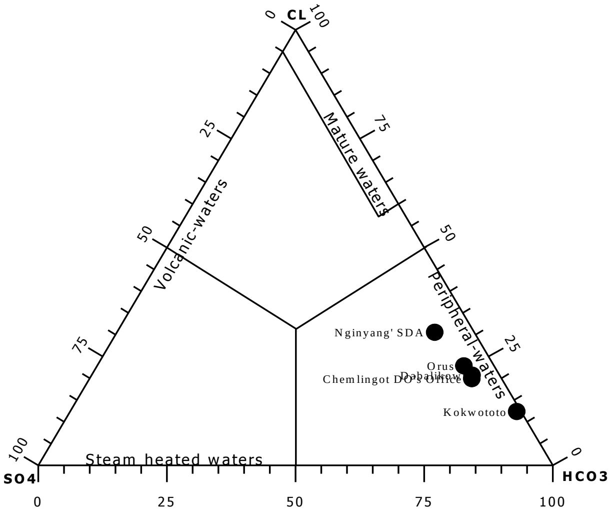

Figure 3: Paka boreholes Cl-SO4-$HCO_3$ ternary diagram

All the borehole waters indicate these are mixed sodium bicarbonate-chloride waters which could have derived from interaction between sediment deposits with thermal waters discharged in the boreholes.

### 4.2 Mixing trends of water in Paka geothermal prospect

Mixing plots involving chloride, boron, magnesium, sulphate, and enthalpy were plotted in Figures 4, 5, 6 and 7 respectively. These indicate linear trends due to compatibility of some of the constituents. Water formed by mixing of geothermal water and cold ground water or surface water possesses many chemical characteristics which serve to distinguish it from unmixed geothermal water. The chemistry of geothermal water is characterized by mixing and equilibrium conditions between solutes and alteration minerals, whereas the composition of cold waters appears mostly to be determined by the kinetics of leaching process.

The main chemical characteristics of mixed waters, which serve to distinguish them from equilibrated geothermal waters, include relatively high concentrations of silica in relation to the discharge temperature, low pH relative to water salinity (often in the range 6-7 for Cl concentrations of less than 100 ppm) and high carbonate, at least if the mixing has prevented boiling and the temperature of the hot water component exceeds some 200 ˚ C. Linear relationships of between chloride on the one hand and boron on the other can be very handy in upflow zones. Figure 4 shows the mixing plot involving chloride vs boron concentrations.

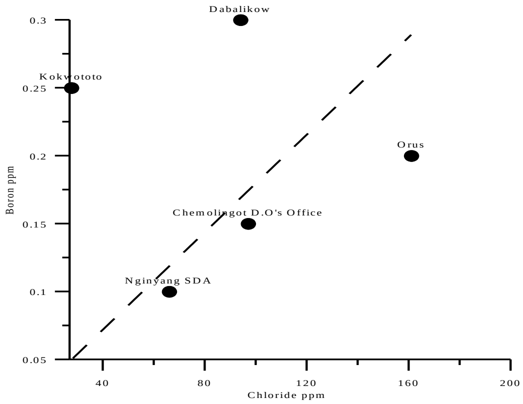

Figure 4: Chloride and boron contents of waters sampled from the Paka geothermal prospect. The broken line is obtained by a linear regression of the data.

Under normal circumstances chloride and boron levels in cold water are as a rule, low but much higher in geothermal waters. These constituents are not considered to be incorporated in geothermal minerals, mixing involves simple lowering of concentrations without affecting the Cl/B ratio. The mixing trend indicated by chloride- boron plot suggests that at the intersection of the boron and chloride where boron is 0 chloride is much more than could be anticipated. This trend suggests at least partly, there could have been boiling prior to mixing.

Another mixing plot that could be used is the chloride vs sulphate concentrations plot. This is shown in Figure 5.

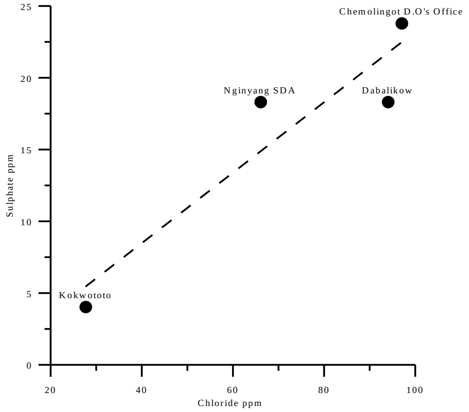

Figure 5: Chloride vs sulphate in waters in the Paka geothermal propect.

Sulphate concentration show a good relation with chloride in the waters sampled from the Paka geothermal prospect. It is interesting to observe that the boreholes with higher temperatures also happen to have higher chloride and sulphate concentrations. It might be expected that the hot waters might have relatively high sulphate content in a number of the boreholes and could be a result of sulphide oxidation by atmospheric oxygen. It is assumed that sulphide oxidation occurs in the shallower depths as the deeper hotter fluid ascend to the surface and mixes with shallower ground waters to give very modified water composition. It is conceivable that the waters that emerge in the boreholes are mixed waters in which case atmospheric oxygen in the cold water component was involved in converting the sulphide to sulphate.

Figure 6 shows the mixing plot of magnesium vs sulphate.

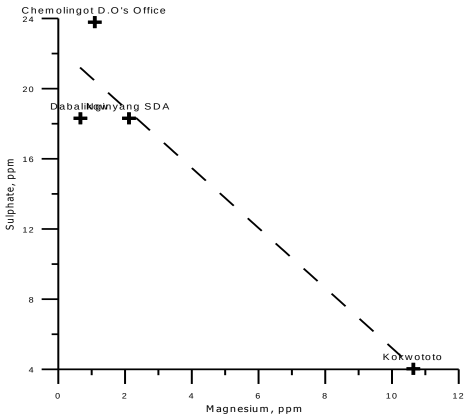

Figure 6: Magnesium vs Sulphate in the waters sampled in the Paka geothermal prospect.

High concentrations of magnesium is a good indicator of ground water or surface water. The Kokwototo borehole could be a good indicator of ground or surface waters which could be diluting waters with higher temperatures. The waters with higher temperatures are waters towards the Nginyang' or Chemlingot area which could have a higher concentration of sulphate as a result of oxidation of sulphide by atmospheric oxygen. The dilution trend could be occurring in an East-West direction from Kokwototo to Chemlingot. This could partly determine the hydrology of the Paka geothermal system. A chloride-enthalpy mixing plot is shown in Figure 7.

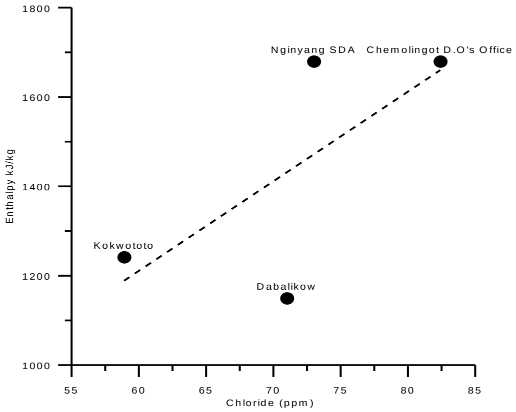

Figure 7: Chloride- enthalpy mixing diagram. Enthalpy was derived from Na-K geothermometry temperatures.

The chloride – enthalpy plot takes into account both mixing and boiling processes. It involves relating analysed chloride levels to water enthalpy. The enthalpy can be derived in a number of ways, such as from measured discharge temperatures, geothermometry temperatures and silica- enthalpy mixing model temperatures. The enthalpy of the waters in this particular case was derived by use of the NaK geothermometry from (Fournier, 1979 and Giggenbach, 1988). The mixing pattern of the chloride-enthalpy plot is consistent with the other mixing plots. The plot depicts that hotter water, probably represented by those sampled at Chemlingot have the highest temperatures and chloride. The mixing trend suggests that the water is being diluted from Chemlingot on the western part of the prospect towards Kokwototo on the eastern part of the prospect. This could partly contribute to the mixed nature of the waters discharged by boreholes in this prospect in addition to interaction by sediment deposits.

## 4.4 Solute geothermometry

Fluid geothermometry is an important facet of the geochemistry of thermal areas and relies on the fact that temperature dependent reactions are solely responsible for the concentration of certain mineral phases in particular certain elements. The use of cation and silica–based geothermometry is based on the assumption that chemical equilibrium is obtained between water and rock at elevated temperatures. Application of these geothermometers to thermal waters in the Paka geothermal prospect area was constrained by the fact that most of the dissolved solids load in these waters appear to have been acquired by evaporite dissolution rather than by interaction between water and rock in its more limited sense. An attempt was made to apply various geothermometry functions to the thermal waters sampled in the prospect area. The thermal waters were evaluated using the sodium-potassium-magnesium ternary diagram for suitability of solute geothermometry application. This is shown in Figure 8.

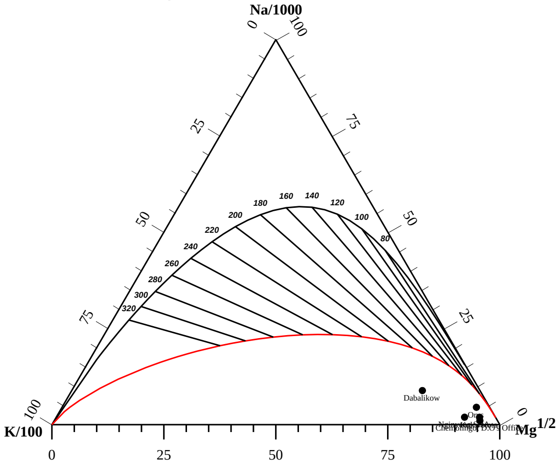

Figure 8: Evaluation of Na-K-Mg content of borehole waters from Paka geothermal prospect

A number of limitations can be noted when some of these solute geothermometers are applied. The Na-K geothermometers are best applied to thermal waters that are chloride rich. For lower temperature waters which have had long residence times the NaK function may be applicable. It can give indications regarding the deeper parts of the system in comparison to silica-quartz geothermometer. The Na-K-Ca geothermometer works under the same conditions as the Na-K but extends the temperature range down to between 120 ˚ and 200 ˚ C. Quartz temperature is best applied for reservoir conditions greater than 180 ˚ C. The functions applied for Na-K, Na-K-Ca and Tqtz are as follows;

$$t^0C = \frac{1217}{Log(Na/K) + 1.483} - 273$$ Na-K ( Fournier, 1979) 1

$$t^0C = \frac{1390}{Log(Na/K) + 1.75} - 273$$ Na-K ( Giggenbach, 1988) 2

$$t^0C = \frac{1647}{Log(Na/K) + \beta\left[\log(Ca^{1/2}/Na) + 2.06\right] + 2.47} - 273$$

Na-K-Ca ( Fournier & Truesdell, 1973) 3

The following considerations apply in the application of this geothermometer:

i) Calculate $\left[\log(Ca^{1/2}/Na) + 2.06\right]$; if its value is positive, then use β=4/3in the formula in determining the temperature. If that calculated temperature is < 100˚ C, then this temperature is appropriate.

ii) If the β=4/3 calculated temperature is > 100˚C or $\left[\log(Ca^{1/2}/Na) + 2.06\right]$ is negative, then use β = 1/3 to calculate the temperature.

$$t^{o}C = -4.2198\,E01 + (S)*2.8831\,E-01 - (S^2)*3.6686\,E-04 + (S^3)*3.1655\,E-07 + (\log_{10} S)*7.7034\,E01$$ 4

S=Concentration of silica in mg/kg
tqtz (Fournier and Potter, 1982 a)

Table 3a shows solute geothermometry temperatures (Fournier, 1979; Giggenbach, 1988; Fournier and Truesdell, 1973 and Fournier and Potter, 1982 a).

Table 3a: Aqueous geothermometry temperatures from Paka geothermal prospect.

| Site | Na-K ( F, 1979) | Na-K (G, 1988) | Na-K-Ca ( F & T, 1973) | Tqtz F&P 1982a |
|---|---|---|---|---|
| Nginyang SDA | 348 | 351 | 266 | 126 |
| Orus | 182 | 200 | 164 | 79 |
| Dabalikow | 250 | 263 | 209 | 101 |
| Kokwototo | 270 | 281 | 221 | 97 |
| Chemolingot D.O's Office | 348 | 351 | 265 | 97 |

The Na-K geothermometry temperatures for the borehole waters yield very high temperatures. These range from 182 to 351 ˚ C for the borehole water in Orus to those in Nginyang' and Chemlingot D.O's office using the Na-K function by (Fournier, 1979). These geothermometry temperature compare quite well with those of the Na-K function (Giggenbach, 1988). The Na-K-Ca geothermometer provides temperatures that are lower than the Na-K function. Under normal conditions the Na-K-Ca geothermometer usually gives slightly higher temperatures than the Na-K geothermometer for boiling hot spring waters. Loss of potassium from solution will lower the Na-K-Ca temperatures. Loss of calcium will counter potassium loss through precipitation. Probably some loss of potassium through feldspar precipitation could cause potassium to decline in concentrations. The Na-K-Ca geothermometer gives lower temperature than those of Na-K. The Na-K-Ca geothermometry temperatures were highest in samples from Nginyang' S.D.A and Chemolingot D.O's office boreholes while they were lowest at the Orus borehole. The quartz equilibrium temperatures by (Potter and Fournier, 1982) yield much lower geothermometry temperatures. This was probably due to the silica content of the thermal water which has not equilibrated with the mineral in the rocks due to low temperatures of the water discharged from the boreholes. Mixing and dilution trends could probably contribute to the differences in the temperatures yielded by the quartz temperatures. A relationship between tNaK and tqtz was ploted and is shown in Figure 9:

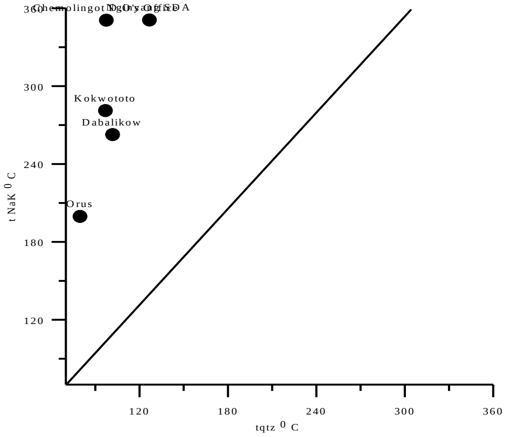

Figure 9; Relationship between quartz equilibrium and Na-K temperatures.

In the most cases results of chemical geothermometry for mixed waters from warm springs and boiling springs differs. Na-K temperatures for mixed warm thermal waters are equal to or higher than quartz equilibrium temperatures. In Figure 10 the thermal waters from the boreholes in the Paka prospect all have NaK temperatures much higher than the quartz equilibrium temperatures. In situations like this it is often interpreted that the major cation concentrations in the warm mixed waters are governed by leaching after mixing (Arnorsson, 1985). The Na-K and N-K-Ca geothermometry temperatures for the boreholes may be unrealistic since they were based on the assumption that fluid mineral equilibrium is approached. This assumption may not be valid.

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