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# A Comparison Between Silica and Cation Geothermometry of the Malawi Hotsprings

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## ABSTRACT

Malawi is one of the poorest countries in the world and one of the most densely populated in south-eastern Africa. Its major power source is hydro-electricity. During the past few years, the power generation capacity has been reduced, which has impacted negatively on the socio-economic development of the country. The country holds an enormous potential to generate geothermal energy due to the country`s position within the Great African Rift valley. This could contribute to economic growth, poverty reduction and technological development in Malawi. The paper presents findings of research on comparisons between silica (quartz and chalcedony) and cation geothermometers (Na-K, Na-K-Ca and K-Mg) of hot springs in the Malawi Rift, in order to deduce the temperature at depth of selected hot springs. The saturation indices of most springs have a bearing on the geology of the areas where these hot springs are found. The Na-K geothermometers are, in general, higher than the Na-K-Ca geothermometer and the K-Mg geothermometer shows temperatures that are too low to be considered. The difference in the results between the different geothermometers may indicate shallow conditions of mixing with groundwater. Results also indicate that some hot springs have sufficient heat-generating capabilities and warrant further exploration work to assess their suitability for energy generation.

## 1. INTRODUCTION

The crustal movement of fluids is an important factor in heat transfer and mass transport, which leads to the formation of many ores and metals of economic significance. The typical manifestation of deeply circulating fluids is the occurrence of hot springs. One of the major tasks in the exploration of geothermal resources is to estimate subsurface temperature in the reservoir from the geochemical and isotopic composition of thermal springs. The most commonly used geothermometers are the silica (quartz and chalcedony), the Na-K and the Na-K-Ca relationships (Fournier, 1973; Fournier and Truesdell, 1973; Ellis and Mahon, 1977; D'Amore and Arnórsson, 2000).

The goal of this study is to deduce the temperature at depth of selected hot springs in order to promote the exploration of geothermal energy as an alternative source of power in Malawi. Geothermal energy is important because it is a renewable energy source; it protects the environment and conserves natural resources. Its exploration could contribute to economic growth, poverty reduction and technological development in Malawi.

Silica, Na-K, $K^2$-Mg and Na-K-Ca geothermometers were used in order to deduce the deeper water equilibrium temperature of the source aquifer in the Malawi's hot springs. The subsurface temperatures were inferred through chemical data compiled from previous studies (Bloomfield and Garson, 1965; Harrison and Chapusa, 1975; Ray, 1973). The springs in the studied zone are associated with the major rift faults of the western branch of the East African rift system, which control the geometry of the Cenozoic Malawi Rift (Bloomfield and Garson, 1965; Ray, 1973, Dulanya et al., 2007). Calcium-sodium-magnesium bicarbonate groundwaters predominate throughout the country (Carter and Bennett, 1973). These types of waters are common in the Rift Valley zone.

## 2. GEOLOGICAL AND HYDROGEOLOGICAL SETTING

### 2.1 Geological Setting

Malawi is situated in S.E. Africa (Fig.1) within the western branch of the East African Rift System (EARS). It is within latitudes 9°S and 18°S and longitudes 32°E and 36°E.

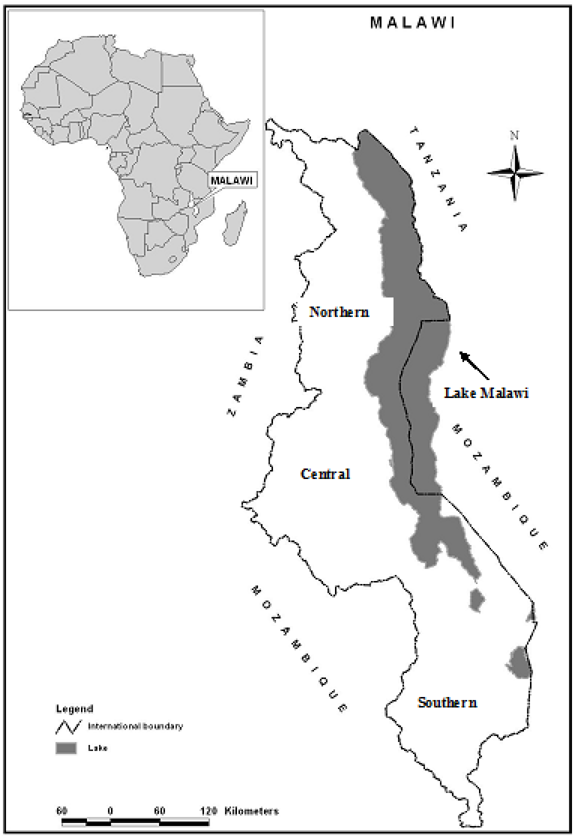


**Figure 1: Map of Malawi and neighbouring countries.**

The geology of the country (Fig. 2) is summarised in Carter and Bennet (1973). It is dominated by Precambrian to Lower Palaeozoic high-grade metamorphic rocks belonging to the amphibolite and granulite facies. These rocks have pelitic and semi-pelitic affinities. Intercalated within these pelitic rocks are calc-silicate gneisses and marbles, some bands of amphibolites and basic and ultrabasic assemblages, e.g. pyroxenites, serpentinites and metagabbros. Overlying the Lower Palaeozoic rocks are the Karoo sedimentary rocks that are best developed in troughs found in the northern and southern parts of the country. Examples include sandstones, limestones and mudstones with coal formations. The climax of the Karoo in the south was the eruption of volcanic rocks such as basalts and dolerites. The Jurassic to Cretaceous period saw the emplacement of alkaline igneous rocks including granites, syenites, carbonatites, agglomerates, foidolites and associated alkaline dykes. These rocks are best developed in the southern part of the country. The Cretaceous was a transition period between the Karoo rifting and the formation of the Recent East African Rift System (Castaing, 1991). It seems that tectonics in the area have acted at different times, the oldest being at 2000–1400 m.y; the youngest still active today. These are considered to be mainly due to the reactivation of NW-SE structures (Tiercelin et al., 1988), which resulted in the creation of NE-SW troughs (Castaing, 1991). The Tertiary and Quaternary are developed along the major drainage systems including Lake Malawi, and includes alluvial sediments. Pleistocene volcanicity is found in the northern part of the country, and this is an extension of the Rungwe volcanic province from southern Tanzania. Epeirogeneic movements related to the rift faulting are the dominant feature of the geology.

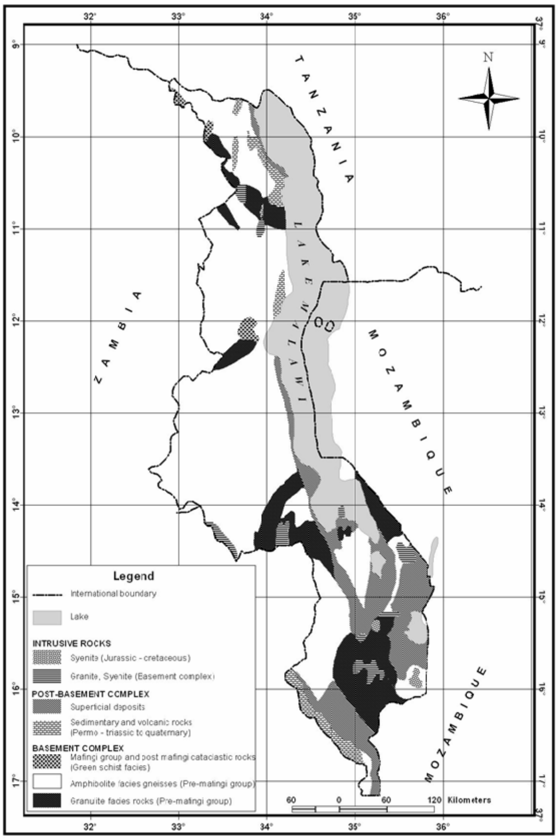


**Figure 2: Geology of Malawi (modified after Carter and Bennett, 1973).**

### 2.2 Hydrogeological Setting

Malawi's hot springs (Figure 3) were known as early as the dawn of the last century and are described by various authors (Bloomfield, 1965a; Bloomfield and Garson 1965; Garson 1960; Ray 1973; Harrison and Chapusa 1975; Dulanya 2006; Dulanya et al. 2007). Previous work on these thermal springs mostly focussed on mapping the litho-structural controls and their physico-chemical characteristics.

The location of the hot springs tends to be clustered along or near the intersections between the major fault systems (NW and some NE-trending Cenozoic to Recent faults) within the Rift Valley areas. These areas are of low altitude with an annual mean temperature of 23 to 25.5ºC and an annual mean rainfall of less than 900 mm (Nkhata, Pers.Comm.). Most of the hot springs have a strong sulphurous smell and some have been polluted by human and animal usage (Dulanya, 2006).

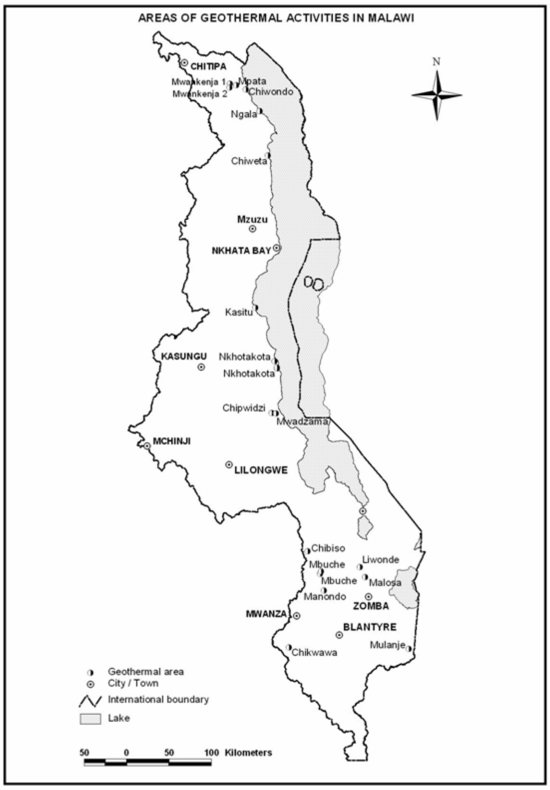


**Figure 3: Areas of geothermal activity in Malawi.**

The aquifers in the country are either classified into alluvial or basement aquifers. The basement aquifer is generally shallower than the alluvial. According to Nkhata (Pers.Comm.), the water tables are first encountered at about 15 m – 18 m. for most of the areas (alluvial and/or basement aquifers) and may represent some perched aquifers. Hot springs have been mapped in the basement, alluvium and even in Karoo rocks. Borehole depths for the alluvial aquifers are mostly at about 45 m and the basement aquifers approximately 40 m. Carter and Bennet (1973) have found that calcium-sodium-magnesium bicarbonate groundwaters predominate throughout the Rift Valley. Cation exchange and the mineralogy of the aquifer are the main factors determining the water composition. The deposits of the Rift Valley zone coincide with erosional and depositional surfaces of Quaternary age. Little is known of the groundwater potential of the Karoo formation that crop out in the northern and southern parts of the Rift Valley.

## 3. METHODOLOGY

### 3.1 Water Sampling and Analysis

Since October 2003, the Geological Survey Department of Malawi has been trying to review the hot spring resources of the country. A Global Positioning System (GPS) has been used to document the location of the various hot springs. Results were downloaded, computed and plotted on a base map.

Physico-chemical data was compiled from previous studies (Bloomfield and Garson, 1965; Garson, 1960; Ray, 1973; Harrison and Chapusa, 1975) by the University of Malawi. The sampled water were analysed for $SiO_2$, Ca, Mg, Na, K, $SO_4$, $HCO_3$, Cl (Table 1), acidity, alkalinity, and electrical conductivity. (For more information about the sampling techniques, chemical analysis and analytical procedure see the studies mentioned above). Determination of most metals was done using Atomic Absorption Spectrophotometry (AAS), while carbonates and bicarbonates were analysed by titrimetry, sulphate and chloride by gravimetric (turbidimetric) methods. The pH of water samples was done at sampling points using a pH meter. Before determining the pH, the meter was calibrated using pH 7 and pH 4 buffering solutions, respectively. The electrode of the meter was rinsed with distilled water before determining the pH of any subsequent sample to prevent inter-sample contamination. Electrical Conductivity (EC) was determined in the field using a conductivity meter. The electrode of the meter was rinsed before dipping into subsequent water samples to prevent inter-sample contamination.

**Table 1: Selected physico-chemical analysis of some hot springs (after Dulanya, 2006).**

| SPRING | pH | Eh | T °C | $SiO_2$ | Ca | Mg |
|---|---|---|---|---|---|---|
| Chinuka1 | 7.5 | 8.4 | 29 | - | 16 | 1.9 |
| Chinuka2 | 8.1 | 6.8 | - | - | 18 | 3.5 |
| Mwankenja1 | 8.2 | 6.4 | - | - | 5 | 12 |
| Mwankenja2 | 7.8 | 6.2 | 53.4 | 70 | 6.8 | 6.2 |
| Mwankenja3 | 8.5 | 7.4 | 50.1 | 42 | <1 | 7 |
| Vungu | 8.6 | 6.1 | 38.2 | 70 | 3.2 | 4.8 |
| Mpata1 | 8.7 | 5.6 | 46 | 70 | 1.6 | 1 |
| Mpata2 | 9 | 6.9 | 50.1 | 44 | <1 | 2 |
| Nkhota kota | 8.7 | *505 | 65 | 90 | 4.4 | 0.7 |
| Chipwidzi | 9.5 | *485 | 52.4 | 80 | 2.4 | 0.5 |
| Liwonde1 | 9.1 | $^{1}$0.30 | - | Nd | - | - |
| Liwonde2 | 9.1 | 0.37 | - | 48 | - | - |
| Manondo | 7.8 | - | 38 | - | 12 | 6.7 |

*Values are in ppm: nd → not detectable*
*Eh: unit of measurement is µmhO/m x $10^2$*
**RM/$cm^3$ - 20ºC*

### 3.2 Groundwater Chemistry

The triangular plots for the major cations (Figure 4a) and anions (Fig.4b) were used to map water types. Saturation indices (SI) for minerals most representative of the aquifer were calculated using the PHREEQC program (Parkhurst and Appello, 1999). The saturation index is defined as SI = log ($P_{AI}/K_T$) where $P_{AI}$ is the product of ionic activity of the ions and $K_T$ is the equilibrium constant of the mineral at the spring temperature.

### 3.3 Chemical Geothermometry

Deeper water equilibrium temperatures were inferred from SiO2, Na-K, $K^2$-Mg and Na-K-Ca geothermometers, following the techniques described by Fournier (1973); Fournier and Truesdell (1973); Truesdell and Fournier (1977); Albarede and Hoffman (2003) (See Table 2). The following equations have been used to calculate the temperature in the aquifers:

1) Silica geothermometers

$$T = \frac{1306}{\left(5.19 - \log[SiO_2]_{soln}\right)} - 273.15 \qquad \text{(Silica)}$$

2) Cation Geothermometers

$$T = \frac{1390}{\left(1.750 + \log\left(\frac{[Na^+]}{[K^+]}\right)\right)} - 273.15 \qquad \text{(Na-K)}$$

$$T = \frac{4410}{\left(14.0 - \log\left(\frac{[K^2]}{[Mg]}\right)\right)} - 273.15 \qquad \text{(K-Mg)}$$

$$T = \frac{1647}{\left(\log(Na-K) + \beta[\log(\sqrt{(Ca/Na)} + 2.06] + 2.47\right)} - 273.15 \qquad \text{(Na-K-Ca)}$$

*Where $\beta$ = 1/3*

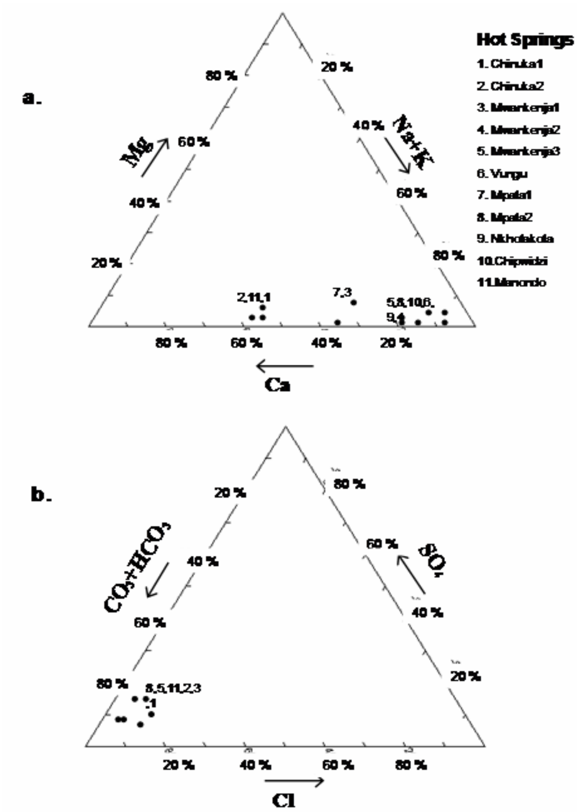


**Figure 4 (a, b): Triangular plots of main cations and anions for hot springs in Malawi.**

## 4. RESULTS AND DISCUSSIONS

### 4.1 Geochemistry of the Hot Springs

The physico-chemical analyses of some selected hot springs (from Dulanya, 2006) are given in Table 1. The temperatures of the springs vary from 29 to 65ºC. Nkhota kota in Northern Malawi seems to show the highest temperature of approximately 65ºC. However, Dulanya (2006) had documented temperatures of around 80ºC in the Chiweta springs. They may be the hottest springs in Northern Malawi and perhaps the entire country. The same author stated that the waters of these springs range from being relatively soft to hard and neutral to basic in pH with very low conductivity. Average pH values of the other studied springs (Table 1) vary between 7.5 and 9.1. According to Kharaka and Mariner (2001), pH values higher than 8.5 indicate dissolution of a significant part of silica.

However, one of the possible origins of these hot springs could be from waters of meteoric origin that circulates deep into the fault zones and rises to the surface once it is heated. The triangular plots for the major cations (Fig. 4a) and anions (Fig. 4b) illustrate that the springs are calcium-sodium- bicarbonate rich waters. From Figure 4a, there are three patterns of clustering of hot springs that can be observed, namely: Ca-richer and Na+K-poorer; Ca-poorer and Na+K-richer; and a third cluster that is intermediate. Based on these results, these waters can be classified as Ca-Na-K-(Mg) – $HCO_3$. These results reflect local variations in the geological formations and hydrochemical processes governing the quality of these groundwaters, and are consistent with Carter and Bennett (1973) although more work to establish these processes is required. Sodium and potassium are most likely the result of ion exchange of calcium, and to a lesser extent magnesium from the source rocks. Sodium and potassium are likely to increase away from areas of recharge, along flow paths.

Ionic strengths and saturation indices are shown in Table 2. Results indicate that most of the hot springs are supersaturated (SI>0) with respect to chalcedony and quartz, and undersatured with respect to calcite, dolomite, anhydrite and gypsum. There is a predominance of calcium and magnesium in most of the aquifers. Although most of the hot springs in the Malawi Rift are within areas covered by recent superficial cover, the SI values may indicate that some of the hot springs emanate from deeper lithological units and are suggestive of the geological formations through which these waters pass. The northern Malawi hot springs, for example Mwankenja, Vungu and Mpata, all have SI>0 for calcium and magnesium. The alluvial cover in the areas where these springs are found is underlain by Karoo to Miocene and Pleistocene sedimentary sequences of high permeability comprising sandstones, marls and limestones (Carter and Bennet, 1973). In addition, these rock units are extensively jointed and faulted and contain constituents which are highly soluble in meteoric water. The Basement rocks, on the other hand, are less soluble except for small amounts containing marbles. In this work, the limestones and marls are interpreted to be the principal contributors of calcium and magnesium bicarbonates, while sodium and potassium bicarbonates are derived from the grits and arkoses which are rich in feldspar. These results are consistent with those obtained for the Lower and Middle Shire areas (Habgood, 1966) to the south of the country, where similar lithological assemblages exist.

Although the hydrogeological potential of the Karoo formations is little known, these results seem to suggest that the aquifers in these formations are bicarbonate-rich, just like those from the basement and alluvial aquifers as reported by Carter and Bennet (1973). The Nkhota kota, Chipwidzi and Manondo hot springs, on the other hand, would qualify for basement aquifers, and it is thought that the high Mg and Ca are derived from Talc-Tremolite and other altered ultra-basic and basic rocks which form an integral part of the basement complex rocks in these areas.

### 4.2 Geothermometry

In the present work, silica and cation geochemical results from Table 1 have been used to calculate temperatures of the source. Table 3 is a summary of the results obtained from these computations.

Fig. 5 below shows the graph of equilibration temperatures of silica solutions. The trend line shows an exponential increase, which is expected (Albarede and Hoffman, 2003) of such solutions and could be used to estimate temperature conditions based on silica concentration in a given solution.

**Table 2: Ionic Strength and Saturation Indices of different hot springs.**

| SPRING | **IONIC STRENGTH** | SATURATION INDICES | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** |
| Chinuka1 | 0.0655 | -0.39 | -1.30 | -3.22 | -3.02 | -6.70 | | | | | |
| Chinuka2 | 0.00689 | 0.12 | -0.11 | -2.90 | -2.68 | -6.69 | | | | | |
| Mwankenja1 | 0.00658 | -0.22 | 0.29 | -3.32 | -3.10 | -7.03 | | | | | |
| Mwankenja2 | 0.00845 | -3.56 | | -3.56 | -3.54 | -6.79 | 0.31 | 0.66 | 0.63 | 5.28 | 8.52 |
| Mwankenja3 | 0.007802 | | | | | -7.11 | 0.08 | 0.44 | 3.87 | 8.03 | |
| Vungu | 0.008353 | | | -3.84 | -3.68 | -6.75 | 0.43 | 0.82 | 3.39 | 8.12 | 12.13 |
| Mpata1 | 0.00762 | | | -4.05 | -3.95 | -6.87 | | 0.7 | 2.77 | 7.38 | 14.01 |
| Mpata2 | 0.00723 | | | | | -7.09 | 0.02 | 0.38 | 5.01 | 9.05 | |
| Nkhota kota | 0.0073 | | | -3.27 | -3.38 | | 0.22 | 0.54 | 4.34 | 8.93 | 18.32 |
| Chipwidzi | 0.00734 | | | -3.68 | -3.63 | -6.72 | 0.05 | | 6.82 | 10.80 | 23.48 |
| Manondo | 0.00575 | -0.39 | -0.57 | -3.11 | -2.95 | -6.70 | | | | | |

**1.** Calcite ($CaCO_3$); **2.** Dolomite ($CaMg(CO_3)$); **3.** Anhydrite ($CaSO_4$); **4.** Gypsum ($CaSO_4.2H_2O$); **5.** Halite (NaCl); **6.** Chalcedony ($SiO_2$); **7.** Quartz – ($SiO_2$); **8.** Chrysotile ($Mg_3Si_2O_5(OH)_4$); **9.** Talc ($Mg_3Si_4O_{10}(OH)_2$); **10.** Tremolite ($Ca_2Mg_5Si_8O_{22}$)

**Table 3: Results from Silica and Cation geothermometers compared with the original thermometer results.**

| SPRING | Temp (°C) Thermometer | Temp (°C) $SiO_2$ | Temp (°C) Na-K | Temp (°C) $K^2$-Mg | Temp (°C) Na-K-Ca |
|---|---|---|---|---|---|
| Chinuka1 | 29 | - | 182.4 | 75.8 | 143.7 |
| Chinuka2 | - | - | 213.6 | 79.6 | 164.6 |
| Mwankenja1 | - | - | 149.1 | 39.7 | 124.9 |
| Mwankenja2 | 53.4 | 117.3 | 106.8 | 51.4 | 104.0 |
| Mwankenja3 | 50.1 | 93.0 | 131.5 | 45.0 | 131.9 |
| Vungu | 38.2 | 117.3 | 95.2 | 48.8 | 99.0 |
| Mpata1 | 46 | 117.3 | 91.4 | 62.5 | 99.3 |
| Mpata2 | 50.1 | 95.1 | 116.3 | 50.7 | 118.5 |
| Nkhota kota | 65 | 130.5 | 100.2 | 69.0 | 99.5 |
| Chipwidzi | 52.4 | 124.2 | 88.9 | 65.7 | 93.0 |
| Liwonde1 | - | 99.1 | | | |
| Liwonde2 | - | | 182.1 | 57.3 | 142.9 |
| Manondo | 38 | | | | |

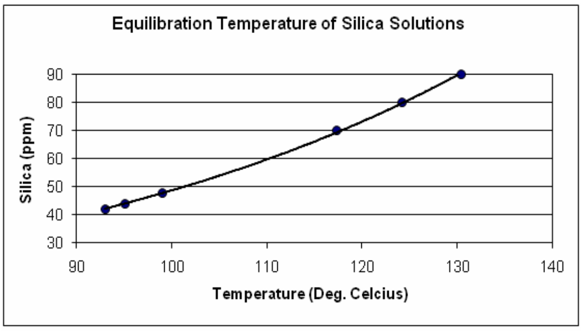


**Figure 5: Equilibration Temperatures of Silica Solutions for some hot springs from Malawi, with trendline.**

A comparison between the various geothermometers is shown in Fig. 6. Silica and the Na-K geothermometer generally indicate temperatures higher than the Na-K-Ca geothermometer, while the K-Mg geothermometer shows too low temperatures to be considered. The difference in the results may indicate shallow conditions of mixing with groundwater. Similar interpretations were made (Dulanya, 2006) by using Eh-pH diagrams. In order to verify the effect of some near surface processes such as water mixing, further studies are recommended.

Finally, using the Na-K geothermometers, it is observed that the hottest hot spring is Chinuka with a subsurface temperature of about 214° C, followed by Liwonde. These results are inconsistent with those obtained using thermometers (Harrison and Chapusa, 1975) which showed that the Nkhota kota springs were the hottest, while Dulanya (2006) observed that the Chiweta springs (results not used in this report) were the hottest. These results could be an effect of meteoric waters which contain dissolved components different from those in the geological environment and influence the geothermometers. As indicated earlier, these results could also be a reflection of the analytical methods utilised for the various hot springs by the various geochemists, and could contribute to erroneous results and interpretations.

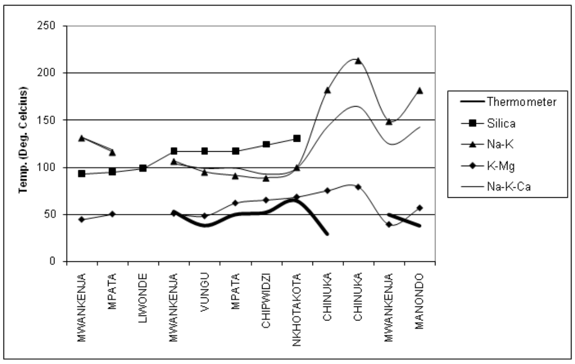


**Figure 6: A Comparison of the different geothermometers.**

However, these results indicate that some hot springs have potential to generate adequate heat, which could be harnessed for energy generation upon further work to prove their viability. This work should also consider, among other things, socio-economic factors that would have impact on energy generation. It is further recommended that re-sampling of these hot springs to confirm the results of this re-interpretation work be ideal as part of further work. Alternatively, other techniques including geophysics to explore these targets could be carried out jointly with the geochemical work.

## 5. CONCLUSIONS

Hot springs occur in several places across Malawi, and they are generally considered to be related to the waning phases of volcanicity associated with the East African Rift systems (Harrison and Chapusa, 1975). According to the hydrochemical data, these springs are calcium-sodium-magnesium bicarbonate groundwaters. Saturation indices of most springs indicated a bearing on the geology of the areas where these hot springs are found.

The Na-K geothermometer shows that the hottest hot spring is Chinuka with a subsurface temperature of about 214$^o$ C, followed by Liwonde with a temperature of 182$^o$ C. The temperature of the springs varies using other geothermometers; this can be due to a consequence of the analytical methods utilized during the sampling of the hot springs.

More studies and sampling of the waters with modern techniques are needed to understand better the relationship between variations in water chemistry, behavior and chemical evolution of these springs, as well as the discrepancy of the results between the different geothermometers. It is also necessary to conduct a detailed study of the water relationship with the tectonic of the area, in order to understand better the geological context where these springs are found.

Geothermal energy could be a good solution to energy deficiency and environment degradation in Malawi. This kind of energy could contribute to the economic growth and poverty reduction. Therefore, the need to identify alternative energy sources need not be overemphasized. The studies also underscore the need for the advancement of science and technology in Africa as a viable solution to alleviating the widespread poverty on the continent. The results indicate that there is unexploited potential for energy generation using the geothermal resources which are clean (less-polluting) and whose supply is very reliable (from natural geological sources). Apart from the current global need for alternative energy sources, the generation of the requisite scientific knowledge for policy generation and implementation amongst African countries is still a key challenge. The results of this work are one such contribution.

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