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CHEMICAL AND ISOTOPIC COMPOSITION OF THERMAL WATERS IN NORTHERN PART OF MALAWI

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ABSTRACT

Geochemical research is an integral part of any geothermal exploration before subsurface investigations such as drilling are performed. The data obtained from geochemical studies is valuable as it gives information about the predicted subsurface temperature and the nature of the geothermal resource. Malawi is conducting the first detailed geothermal investigation in the country, with emphasis on geochemical surveys in the first and second stage. Results obtained during the field campaign which took place in September 2016 were used in this study to trace the origin of thermal waters and predict the subsurface temperature of the Northern Malawi geothermal prospects, as well as to look for favourable chemical characteristics that will enhance future developments. The geothermal prospects of interest include; Chiweta, Kanunkha, Kasitu and Kasanama which form a linear pattern along Lake Malawi. The prospects have similarities in the geological set-up as well as structural set-up. Stable isotopes were used to trace the origin of thermal waters. The thermal waters are meteoric in origin with a slight shift of oxygen for Chiweta samples, probably due to water-rock interaction. Karoo sediments influence the $\text{HCO}_3(\text{SO}_4)$ composition of the thermal waters but the connection between $\text{Cl}(\text{SO}_4)$ composition of the Chiweta samples and rocks is yet to be identified. The thermal waters are partially equilibrated except for Chiweta which is considered mature geothermal water. Subsurface temperatures suggest that Chiweta system has the highest temperature among the prospects with a temperature above 100°C ; the other prospects have temperatures above 70°C . Multiple mineral equilibria supplement the geothermometry results, indicating temperatures within the same range. Calcite and amorphous silica are undersaturated in the systems.

1. INTRODUCTION

Malawi is a landlocked country in south-eastern Africa. It lies between latitudes 8°S and 18°S . Malawi borders Tanzania to the north, Zambia to the north and north-east and Mozambique to the west and south-west. Malawi is located at the southern tip of the western branch of the East African Rift System. Though the country has not been subjected to recent volcanism, it is endowed with some geothermal resources which are non-volcanic (Gondwe, et al., 2015).

1.1 Geological setting of Malawi and the Northern Malawi geothermal prospects

On a large scale, the country is underlain by crystalline Precambrian to lower Paleozoic high-grade metamorphic rocks and igneous rocks in the highlands and plateau areas of the country. The Permian to early Jurassic Karoo super-group, which consists of sedimentary rocks, occupies the fault bounded basins within the Precambrian structural set-up in the northern and southern parts of the country. The Shire valley and the shores of Lake Malawi are overlain by Quaternary to recent alluvial and lacustrine sediments. In the northern part of the country, correlation has been made on the Neogene tuffs inside the northern border of Malawi and Tanzania with an explosive eruption in one of the active volcanoes of the Rungwe volcanic province of the Rukwe Rift. Tuffaceous deposits of the same kind have also been identified in borehole cores of sediments from the northernmost part of Lake Malawi (Gondwe et al., 2015).

The Malawi Rift is largely occupied by Lake Malawi which consists of a series of half grabens, and extends approximately 800 km from the Rungwe volcanic province in southern Tanzania to the middle of the Shire river. It extends a further 600 km to the south by the Urema graben and Dombe trough in Mozambique. Most of the important younger structures, which are significant in search of geothermal systems, are products of Precambrian ductile deformation. Lake Malawi, which dominates the Malawi rift, has three linked half graben basins; Karonga, Nkhatabay and Nkhotakota which are largely controlled by a major bounding faulting system. In the southern part of the country, tectonic features portray a NW-SE trend quite similar to the northern part (ELC, 2016).

2. GEOTHERMAL RESOURCE INVESTIGATIONS IN MALAWI

Geochemical research is an integral part of any geothermal exploration before subsurface investigations such as drilling are performed. In the early stages of geothermal exploration, geochemical studies provide information which neither geological nor geophysical methods can reveal. Most of the manifestations that are dealt with in geochemical studies convey the imprints of the main source, which in this case is the geothermal reservoir. In view of this, during the initial assessment of the geothermal potential of an area, geochemical techniques are mostly used to extract varied information from the source (Giggenbach, 1991). Geochemical studies predict subsurface temperature, identify the origin of thermal fluids, quantify processes that control their compositions and accompanying chemical and mineralogical alterations of rocks (Arnórsson, 2000).

The data obtained from geochemical studies is valuable to any geochemist because during the interpretation of data obtained from various geothermal exploration projects, correct interpretation is the benchmark of success of the overall project. In Malawi, a number of geochemical studies have been carried out throughout the country to get an overall picture of all geothermal manifestations in the country. In one of the studies, Geothermal Development Company (GDC) of Kenya carried out a reconnaissance survey (geochemical survey) of the manifestations on 8th-13th September 2010 with the aim of unveiling the geothermal potential that geothermal resources in Malawi have. The experts collected samples from the manifestations, which were later on analysed in the laboratory to get an overview of the chemical characteristics of the systems. The results suggested temperatures above 100°C of the geothermal systems with the highest temperatures in the Northern part of Malawi. GDC later on recommended to the government of Malawi to carry out detailed surface investigations of the prospect areas (GDC, 2010).

In 2003, prior to the studies conducted by GDC, Geological Survey of Malawi took an initiative to understand the surface expression of the geothermal resources in Malawi and to re-examine the information available in the early 1990s as one way of assessing the suitability of the geothermal energy sources for power generation. Geochemical data was collected and analysed, but a need for thorough research was recommended since the studies done were not comprehensive (Dulanya, 2006).

Fortunately, the Government of Malawi got funding from the International Development Association to assist in the implementation of the Malawi Energy Sector Support Project which aimed at increasing the reliability and quality of electricity supply in major load centres. In order to bring a diversification of energy sources, alternative sources of energy were to be assessed including geothermal sources.

2.1 First detailed assessment of the geothermal resources in Malawi

The assessment of geothermal resources started in early 2016 following the contract signed between Malawi government and Electroconsult (ELC) from Italy. The assessment is expected to end in September 2017. It was planned to consist of three phases, a reconnaissance study, a preliminary appraisal and a pre-feasibility study. The assessment is conducted by the ELC team and local personnel from the Ministry of Natural Resources Energy and Mining. Following the reconnaissance study, around 50 geothermal manifestations had been recorded in the country.

These manifestations proceed from the northern part, where they form a pattern to the southern part of the country where they are scattered with no clear pattern. Figure 1 (ELC, 2016) below shows the location of the manifestations that were encountered during the exercise.

The manifestations in Malawi are hot springs with the highest surface temperatures of 79°C to 84°C. During the assessment, the manifestations were grouped into twenty-four prospects with respect to topographic proximity.

The following six prospects proceeded to the detailed geochemical sampling (preliminary appraisal) which took place in August to September 2016: Chiweta, Kanunkha, Kasanama, Kasitu, Mawira, Chipudzi, and some borehole samples of the Kasungu area. These prospects were chosen based on technical and non-technical parameters such as; maximum temperature, maximum flow rate, temperature loss, oxygen shift, probability of reservoir temperature, structural and hydrological setting and stratigraphy (ELC, 2016).

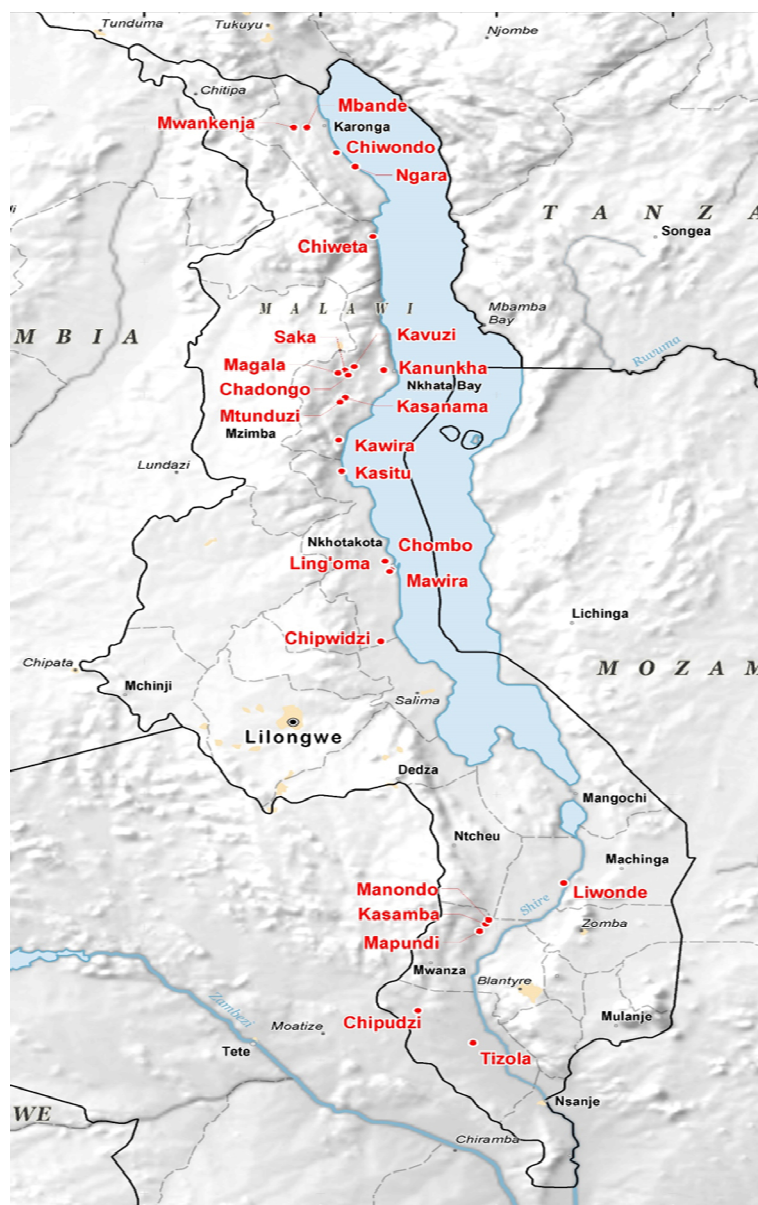


FIGURE 1: Geothermal manifestations in Malawi, red dotted (ELC, 2016)

Among the six chosen prospects that were considered in the preliminary appraisal, only the four that are in the northern region are used in this study, the purpose is to:

- Trace the origin of the thermal fluids.
- Estimate the temperature and utilization potential of the fluids.
- Look for favourable chemical characteristics that will enhance future developments.

The prospects of interests are: Kasanama, Kasitu, Chiweta and Kanunkha.

2.2 Geology of the Northern Malawi geothermal prospects

The geothermal prospects in the northern region are associated with similar rock types with minor contrasts in the geological make up of their surroundings.

Chiweta prospect

Located in Rumphi district, west of Lake Malawi. The area is overlain by basement complex rocks; biotite gneiss, hornblende gneiss and amphibolites, which are mostly south-west trending, delineated by NW-SE and NE-SW faults. The area is also covered by the Karoo sedimentary rocks, which outcrop in a basin. The three major units of Karoo include intermediate beds, yellow mudstones and calcareous siltstones and Chiweta beds. Figure 2 shows the location of Chiweta.

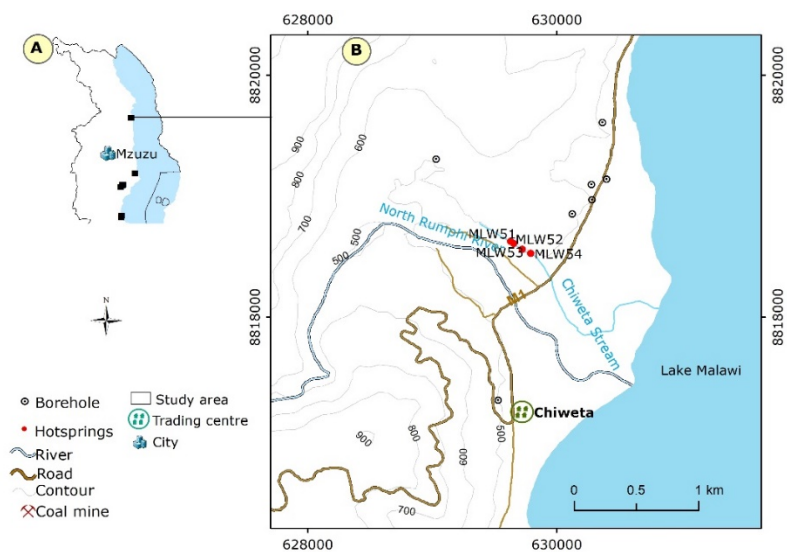


FIGURE 2: Chiweta hot springs (MLW 51)

Kanunkha prospect

Kanunkha prospect is situated in Nkhatabay district as shown in Figure 3. Nkhatabay district has the largest number of thermal manifestations in Malawi. Kanunkha prospect is characterized by a large ridge of the Kondoli mountain chain. The foot wall of the ridge is comprised of recent alluvial deposits and thick levels of loose sediments known as Timbiri beds. The deeply cut gorges of the higher ridges display Precambrian to lower Paleozoic biotite gneiss and biotite-hornblende gneiss. Some mica rich phyllonites bodies cross the gneiss to the south and east of Kanunkha.

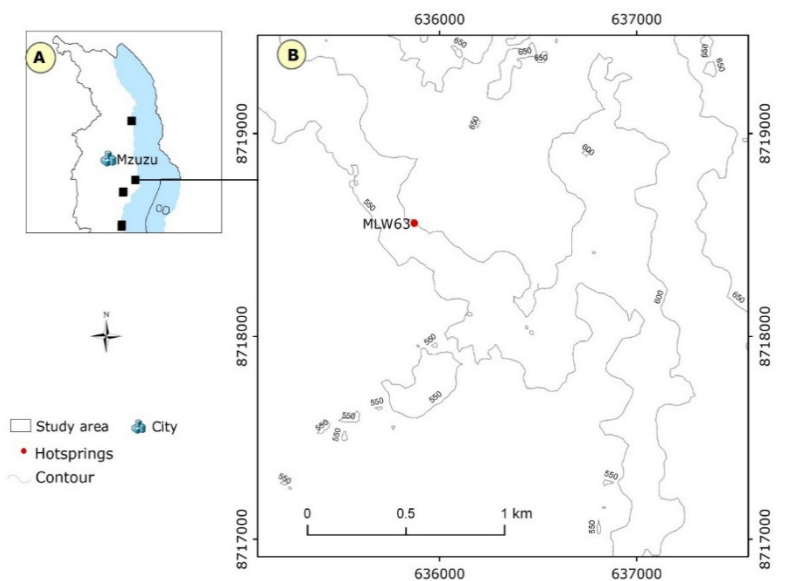


FIGURE 3: Kanunkha hot spring (MLW 63)

Kasanama prospect

Thermal manifestations are found in four localities in Nkhatabay district which were named Kasanama 1, Kasanama 2, Kasanama 3 and Mtunduzi. All the manifestations rest on a 5 km stretch along the Kakwewa river, which is 25 km west of Lake Malawi, as shown in Figure 4x. The upper valley of Kakwewa river is overlain by sedimentary rocks; conglomeritic facies rich in quartz pebbles that belong to the Timbiri beds. Basement complex rocks, mainly biotite gneiss and quartz feldspar gneiss also underlie the area. The flat lowlands of the area are covered by recent alluvial deposits and thick lateritic soil cover. The area also has mica rich phyllonites, which are locally intercalated in the biotite gneiss.

Kasitu prospect

Kasitu is located in Nkhotakota district, and the prospect has two manifestations in total that emerge on the shore of Lake Malawi, as indicated in Figure 5. The manifestations form ponds on the shore of the lake which is overlain by alluvial and lacustrine deposits, colluvial and residual deposits. Basement complex rocks are also noticeable in the area, and consist of biotite gneiss.

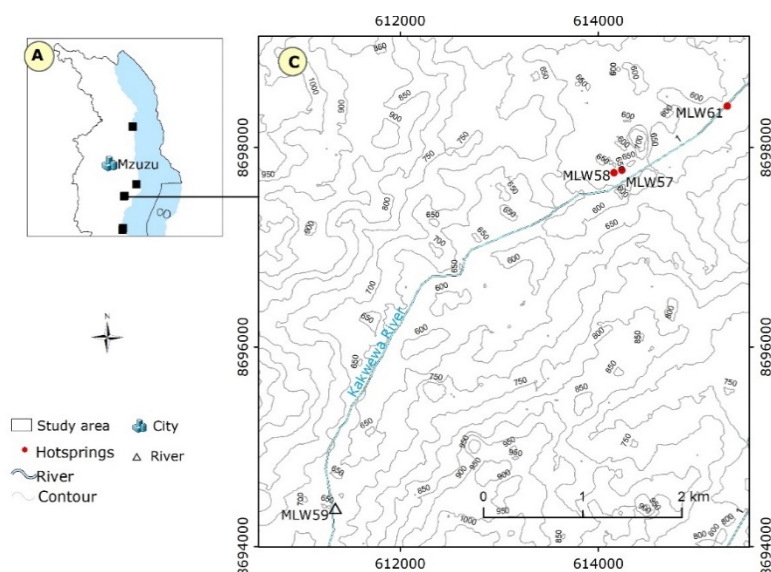


FIGURE 4: Kasanama prospect (MLW 57, 58, 61)

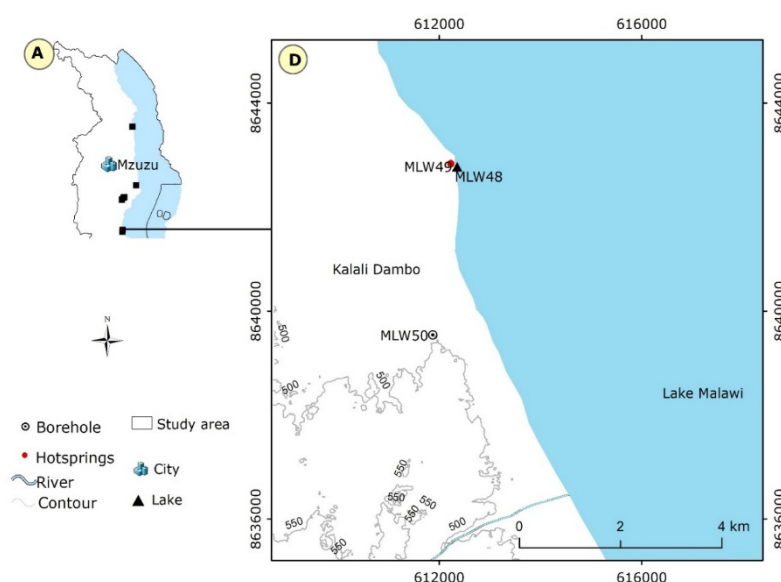


FIGURE 5: Kasitu prospect (MLW 48, 49)

3. METHODOLOGY

3.1 Geochemical sampling

The data used in this study was obtained during stage 2 of the project (ELC, 2016). The geochemical investigations at this stage were conducted in order to scrutinise the six prospects and identify two prospects with the most favourable indications for the last stage of the assessment. The field campaign began on 30th August, 2016 and was concluded on 24th September of the same year. In the course of the preliminary appraisal, 31 rock samples were taken for petrographic analysis and 33 fluid samples were collected. During the preliminary appraisal, emphasis was on geochemical sampling of the six prospects as well as detailed geological mapping.

In the course of the geochemical campaign, the following on-site measurements were made:

1. Temperature measurements using a thermocouple.
2. Total alkalinity by acidimetric titration, which was done on site.
3. Flow rate measurement, which was done where possible using a cone shaped sheet of aluminium.
4. Eh, pH and electrical conductivity by using a portable multi-parametric device with electrodes and standard solutions for calibrations.

In total, 33 water samples were collected from boreholes, rivers and lakes for laboratory chemical and isotopic analyses. The samples were preserved using appropriate treatments such as; filtration, acidification, dilution, and precipitation. Membrane filters with pore size 0.45 µm were used to remove particulate matter. Pure HNO₃ and HCl were added to appropriate samples to preserve cations and dissolved metals and resist precipitation and oxidation. To avoid silica precipitation and polymerisation, dilution and acidification were used.

A few sites were selected for the determination of the ³⁴S/³²S isotopic ratio of dissolved sulfate. Chemical and isotopic analysis of the water samples was conducted in Italy and the United Kingdom. Appendix I shows the geochemical results of the sites that are used in this study.

3.2 Origin and equilibrium state of water

Origin of geothermal waters

Fluids at depth undergo many reactions depending on factors such as the temperature at depth, the composition of the host rock, surface area of the rock available for reaction, permeability and porosity and age of the system, and more. As there are many pathways to the observed alteration, the origin of geothermal waters must be discovered to uncover the processes that led to its alteration (Nicholson, 1993).

3.2.1 Use of stable isotopes

Stable isotopes have a fundamental role in determining the origin of geothermal waters. The stable isotopes of hydrogen (²H and ¹H) and oxygen (¹⁸O and ¹⁶O) are used because of their abundance in water. The isotopic composition is expressed as per mil difference relative to the V-SMOW standard with δ- (per mil) value as:

$$\delta^{18}O = \left(\frac{\left(\frac{^{18}O}{^{16}O} \right)_{sample}}{\left(\frac{^{18}O}{^{16}O} \right)_{standard}} - 1 \right) * 1000 \text{ ‰} \quad (1)$$

$$\delta^2H = \left(\frac{\left(\frac{^2H}{^1H} \right)_{sample}}{\left(\frac{^2H}{^1H} \right)_{standard}} - 1 \right) * 1000 \text{ ‰} \quad (2)$$

From the equations, if a sample of water has a negative value, say -30‰, it means that its isotopic ratio in the sample is 30‰ lower than that of the standard. On the other hand, if a sample has a positive value, its isotopic composition is more enriched in the heavier isotope than the standard. The most commonly used standard for water isotopes is Standard Mean Ocean Water (V-SMOW).

A meteoric line, describing the relationship between δD and δ¹⁸O that applies all over the world $\delta D = 8 \cdot \delta^{18}O + 10$ (Craig, 1961) used together with local precipitation lines, and stable isotope values

in unaltered groundwater of meteoric origin are expected to satisfy this equation. The $\delta^2\text{H}$ ratio in geothermal waters is generally like that of the parent water but the $\delta^{18}\text{O}$ value of the geothermal water is sometimes higher than that of meteoric water. Enrichment of ^{18}O in geothermal fluids relative to meteoric water (oxygen isotope shift) is because of water-rock reactions at depth, which alters the original composition of meteoric water and mineralogy of rocks. In waters that are depleted in ^{18}O ($\delta^{18}\text{O} < 0$) the exchange reactions usually cause a positive isotope shift (towards higher $\delta^{18}\text{O}$) as the rocks are generally more enriched in ^{18}O than the fluids.

3.2.2 Ternary diagrams

Cl-SO₄-HCO₃, ternary diagram:

Classifying the fluid sampled at surface is also one way of tracing the origin of the hydrothermal fluid. The fluids that are found in different geothermal systems are classified based on different factors. For example, the chemical composition of the fluids in high temperature geothermal systems varies from the chemical composition in low temperature systems. Giggenbach (1991) proposed to classify geothermal waters based on the dominant anions. The dominant anions used in the chemical classification of the systems include; chloride (Cl^-), sulphate (SO_4^{2-}) and bicarbonate (HCO_3^-). The waters associated with each dominant anion have specific features that often are due to their origin. Classification of a water based on its dominant anions is commonly done graphically, a simple Cl-SO₄-HCO₃ ternary plot is constructed using the analytical data as follows:

1. Sum the chloride, sulphate and bicarbonate concentrations, where bicarbonate is the total concentration of all carbonate species:

$$\Sigma = \text{Cl} + \text{SO}_4 + \text{HCO}_3 \quad (3)$$

2. Calculate the relative proportion of each component of this sum as a percentage:

$$\% \text{Cl} = (\text{Cl}/\Sigma) * 100 \quad (4)$$

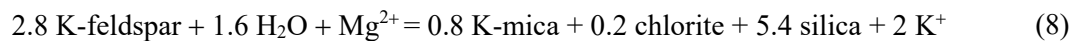
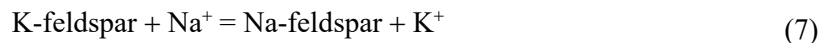
$$\% \text{SO}_4 = (\text{SO}_4/\Sigma) * 100 \quad (5)$$

$$\% \text{HCO}_3 = (\text{HCO}_3/\Sigma) * 100 \quad (6)$$

The ternary diagrams depict the different water types and aids in recognising waters that are suitable for geothermometry and further interpretation. Apart from that, spatial position of the manifestation, mixing trends and sub-surface flow directions can be identified using the plotted data (Giggenbach, 1991).

Na-K-Mg ternary diagram:

A second classification method is by using the Na-K-Mg ternary plot proposed by Giggenbach (1988) to classify waters into fully equilibrated, partially equilibrated and immature waters with respect to all three components and the lithologies associated with the fluids at depth. This method depends on the different rates of the two cation exchange reactions. The ternary plot may also be used to determine the reservoir temperature and best suited geothermometric functions for the equilibrated waters. The plot is based on the following two reactions, where the equilibrium constants depend strongly on temperature:



Due to the different range of concentrations commonly observed in geothermal fluids, the ternary plot is typically constructed using Na/1000, K/100 and $\sqrt{\text{Mg}}$, rather than the actual concentrations. The ternary diagram is constructed using the analytical data as follows, with the total sum of the concentrations:

$$S = C_{\text{Na}}/1000 + C_{\text{K}}/100 + \sqrt{C_{\text{Mg}}} \quad (9)$$

$$\% \text{-Na} = C_{\text{Na}}/10S \quad (10)$$

$$\%K = C_K/S \quad (11)$$

$$\%Mg = 100\sqrt{C_{Mg}/S} \quad (12)$$

Based on the calculations above, the percentages of the three components are plotted on the ternary diagram and the equilibrium state of the waters is then deduced.

3.2.3 Geothermometers

During geothermal exploration, the most commonly used method to estimate reservoir fluid temperature is geothermometry calculations. Geothermometers are therefore valuable tools in the evaluation of new fields and monitoring the hydrology of systems in production. Geothermometers have been classified into three groups (D'Amore and Arnórsson, 2000):

- Water or solute geothermometers.
- Steam or gas geothermometers.
- Isotope geothermometers.

Water and steam geothermometers are collectively called chemical geothermometers. The application of the different geothermometers rests on different assumptions that they are dependent on. Solute geothermometers are further classified into two categories: (1) those which are based on temperature-dependent variations in solubility of individual minerals (e.g. silica); and (2) those which are based on temperature-dependent ion-exchange reactions which fix ratios of certain dissolved constituents (e.g. cations). In this study, solute geothermometers will be used to estimate reservoir temperatures.

The silica geothermometers:

The ones which are most commonly used are quartz and chalcedony. Silica polymorphs that are known in nature include: quartz, amorphous silica, moganite, and tridymite. The silica constituents that control a phase for aqueous silica concentrations solely depend on the dissolution of the primary silicate minerals of the rock and the precipitation of a secondary silica mineral. The dissolution rate of the primary minerals depends on temperature, the chemical properties and how reactive the water is, which is mostly a function of pH.

The basic reaction for the dissolution of silica minerals is expressed as:

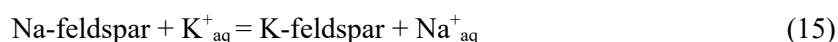


and thus the equilibrium constant for the reaction is:

$$K = (\text{H}_4\text{SiO}_4) \quad (14)$$

Cation geothermometers:

Many cation geothermometers are based on ion exchange reactions of metals (Na-K; Na-K-Ca etc.) most commonly in feldspars, but also in clays, micas etc. High temperature geothermal systems show a temperature-dependent trend variation of sodium and potassium in geothermal waters because of the ion exchange of these elements between co-existing alkali feldspars according to the reaction:



The equilibrium constant for the reaction is:

$$K = (\text{Na}^+)/(\text{K}^+) \quad (16)$$

The geothermometry equations based on the Na/K ratio work well for reservoirs with temperatures between 180°C to 350°C. The reaction also takes place, although at a lower rate, at temperatures as low as 120°C but there the cation concentrations may be influenced by other minerals like clay.

3.2.4 Mineral solution equilibria

Multiple mineral-solution equilibria is a different approach to estimating subsurface temperature. The method involves simultaneously estimating the equilibrium state between a specific water and many hydrothermal minerals as a function of temperature (Reed and Spycher, 1984). By using many components at the same time, the method may overcome some of the problems faced by classical geothermometers, such as sensitivity to gas loss and mixing/dilution with shallow waters that can mask the deep geochemical signatures.

The method solely depends on computed temperature-dependent saturation indices of potential reservoir minerals, by carrying out a full chemical water analysis. To interpret fluid composition based on mineral-solution equilibria, mineral solubility constants (K) are calculated from thermodynamic data and activity products (Q) from analytical data. The latter entails aqueous speciation calculations and end-member mineral activities in solid solutions from their compositions which were analysed.

To predict the state of a mineral, whether stable, forming, or dissolving in water, the mineral saturation index is used. The saturation index of minerals is thus calculated from the following equation;

$$SI = \log \left(\frac{Q}{K} \right) = \log Q - \log K \quad (17)$$

The mineral saturation index is based on the assumption that the saturation index is 0 at the geothermometer temperature. If the saturation index is negative, it follows that the mineral is undersaturated and tends to dissolve (if present). On the contrary, if the saturation index is positive, the mineral is supersaturated and it precipitates as a result.

The computer program WATCH (Arnórsson et al., 1982; Bjarnason, 2010) is used to calculate the chemical composition of geothermal waters, which includes the pH, aqueous speciation, and activity coefficients. Component analysis of the surface geothermal water is the input to the program, including the temperature at which the pH was measured. Concentrations of all species considered in the program are expressed as component concentrations by mass balance equations, and chemical equilibria as mass equations. Distribution of species is attained by solving the equations simultaneously. Ionic strength is then computed and used to re-compute activity coefficients.

Another computer program, PHREEQC (Parkhurst and Appelo, 2013) is also used to perform some aqueous geochemical calculations, in particular speciation and saturation index calculations. The program is based on the equilibrium chemistry of aqueous solutions interacting with minerals, gases, and solid solutions.

4. RESULTS AND DISCUSSION

4.1 Origin and classification of thermal waters in the northern part of Malawi

Based on the isotopic data from the samples that were analysed, most of the waters in the northern region are found to be meteoric in origin as they lie close to the global meteoric water line (Craig, 1961) as shown in Figure 6. The only samples that do not fall on the line are from Chiweta hot springs which show a slight oxygen shift of approximately 0.5-1‰, probably due to oxygen exchange with the host rock. From Figure 6, it is apparent that the Chiweta waters have a different origin than waters from the other three prospects. Furthermore, it is clear that Lake Malawi is not a major source of recharge to any of the geothermal fields. The isotopic values for the lake, 2.33 and 14.9 for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ respectively and the isotopic values of the thermal water samples as shown in Appendix I, denotes that Lake Malawi is not the major source. However, it is possible that Kasanama, Kanunkha and Kasitu fields are fed by the same or similar source.

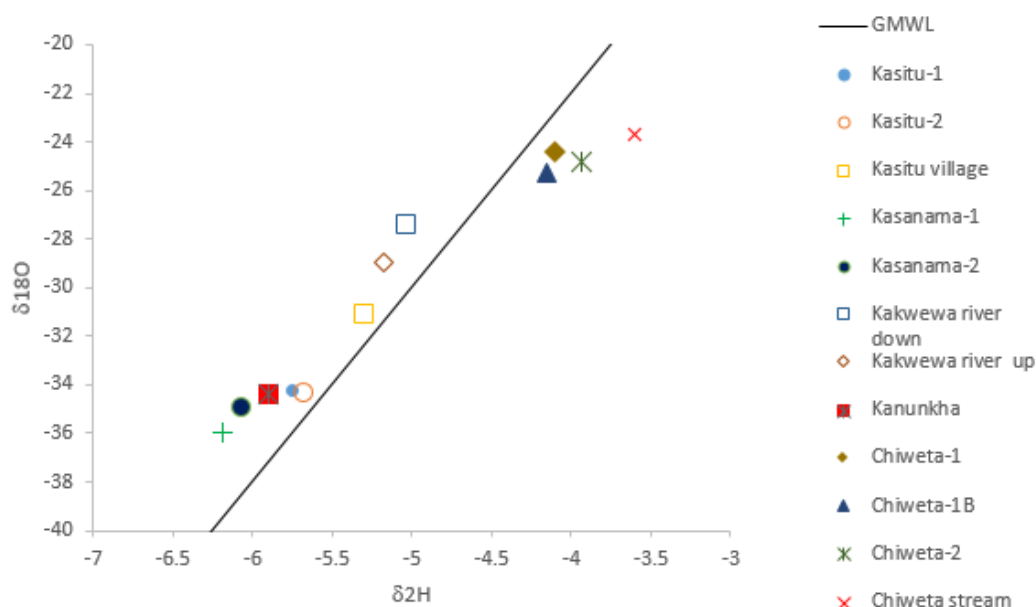


FIGURE 6: Isotope graph for Northern Malawi samples

From the previous report published by the Electro-consult (ELC, 2016), all of the manifestations of Kasanama which are located on the eastern side of Kakwewa river, that is along the foot of the fault plane, are correlated with the fault plane. The fault plane runs several kilometres to the NE-SW, and this gave room for the assumption that the Kakwewa river might be one of the upflow zones of the Kasanama hotsprings. On the contrary, the isotopic plot shows that the samples collected from Kasanama and Kanunkha hot springs are depleted in deuterium compared to the isotopic print of the Kakwewa River, suggesting that the recharge water originates from a higher altitude than the Kakwewa River. This indicates that the recharge of the hot springs may come from the mountainous region which lies to the west of the hot springs. In much the same way, the Kasitu hot springs must have a different origin than the water collected at Kasitu village (borehole).

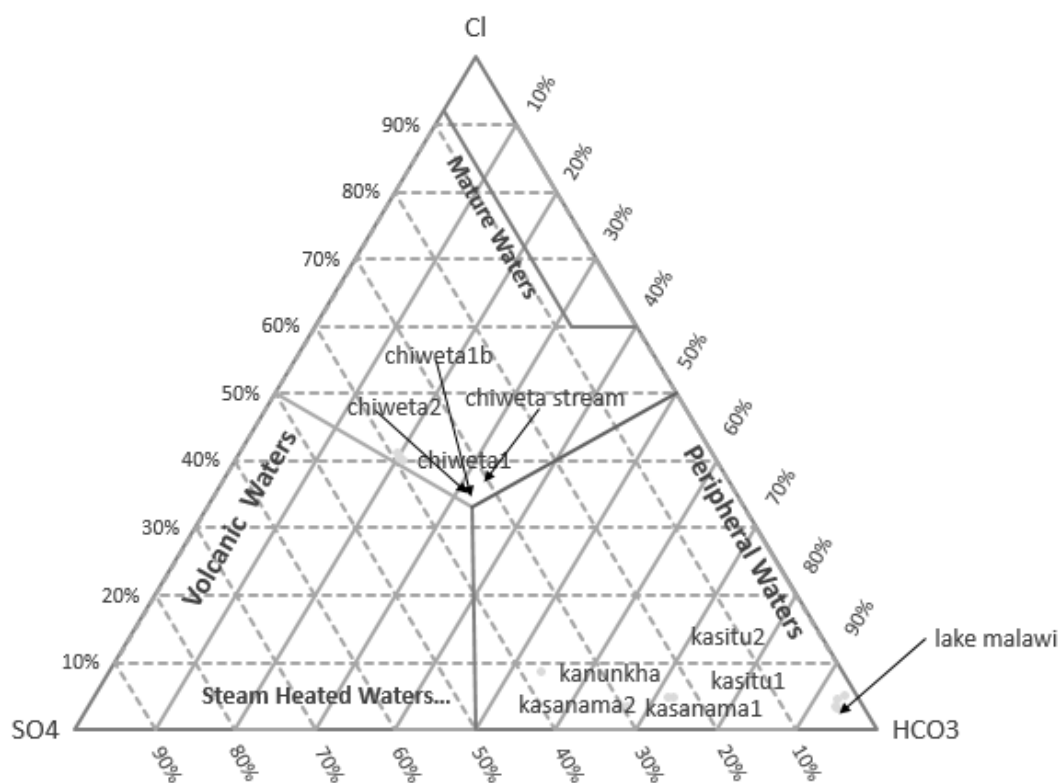
Cl-SO₄-HCO₃ triangular diagram:

The Cl-SO₄-HCO₃ ternary diagram was used to classify the waters into different types based on their dominant anions (Figure 7). In Malawi, the majority of manifestations fall under the HCO₃-SO₄ group, which are often products of mixing or steam and gas condensation, and are commonly known as peripheral waters, some sites have SO₄-HCO₃ waters and only a few have the Cl-SO₄ waters. The Northern region which is an area of interest in this study has HCO₃(SO₄) waters at Kanunkha, Kasitu and Kasanama prospects and Cl(SO₄) waters which were sampled at Chiweta hot springs. Most of the prospects in the northern region are associated with the Karoo sedimentary rocks which were deposited in a nearly north-south trending depression. Prospects situated near the shore of Lake Malawi have these sediments in the north-west and south-east trending depressions. The sedimentary rocks, which are carbon rich, explain the high carbonate content of most the thermal waters along the lake.

Na-K-Mg triangular diagram:

The ternary diagram using the Na-K geothermometer (Arnórsson et al., 1983) and the K-Mg geothermometer (Giggenbach, 1988) was used to classify the waters based on their equilibration state. As illustrated in the Na-K-Mg plot (Figure 8), most of the waters in the northern region are partially equilibrated, these are; Kasitu, Kasanama, and Kanunkha. The waters may have been mixed with magnesium-rich waters along the way to the surface. According to the plot results, Kasanama, Kasitu and Kanunkha may have quite similar temperatures at depth.

Only one site, Chiweta, in the northern region locates itself on the equilibration line and two of the samples are partially equilibrated suggesting that the Chiweta thermal water is more mature and/or less mixed than that from Kasitu, Kasanama and Kanunkha.

FIGURE 7: Cl-SO₄-HCO₃ ternary plot for Northern Malawi samples

All the samples collected from the rivers, lake, and boreholes in some of the areas close to the sampled areas, are considered immature.

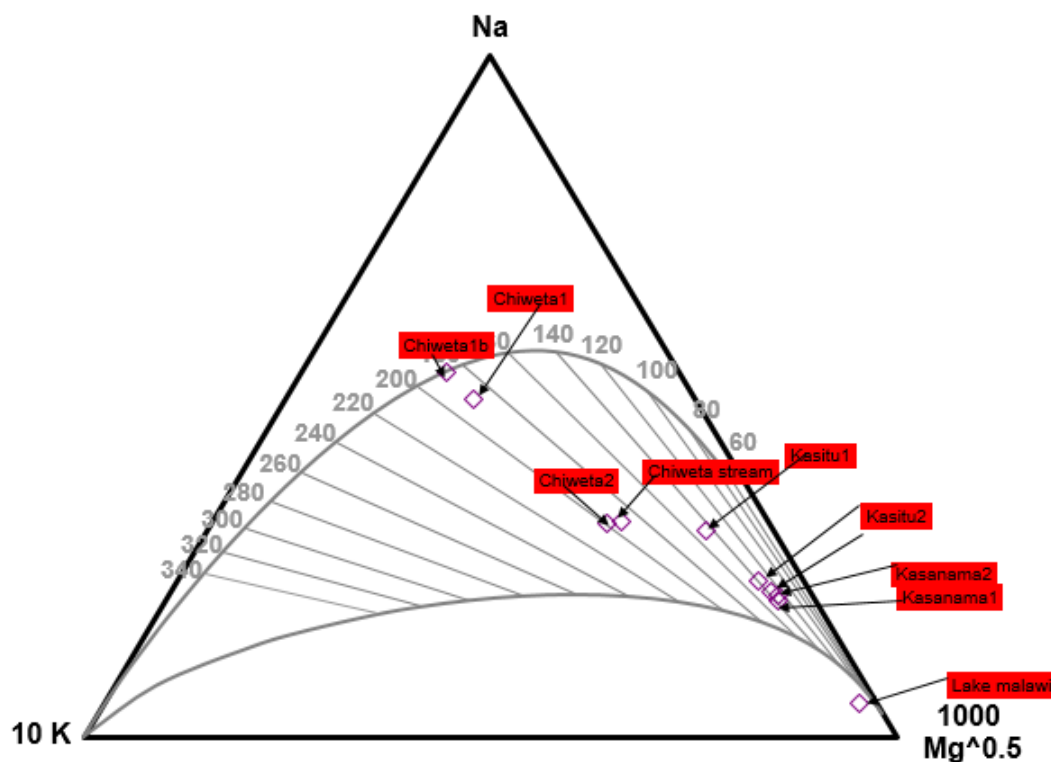


FIGURE 8: Na-K-Mg ternary plot for Northern Malawi water samples

Geothermometry results

Table 1 below shows the geothermometry results for the northern part of Malawi. One cation geothermometer Na/K (Arnórsson et al., 1983) and two silica geothermometers; quartz geothermometer (Fournier and Potter, 1982) and chalcedony geothermometer (Fournier, 1977), were used.

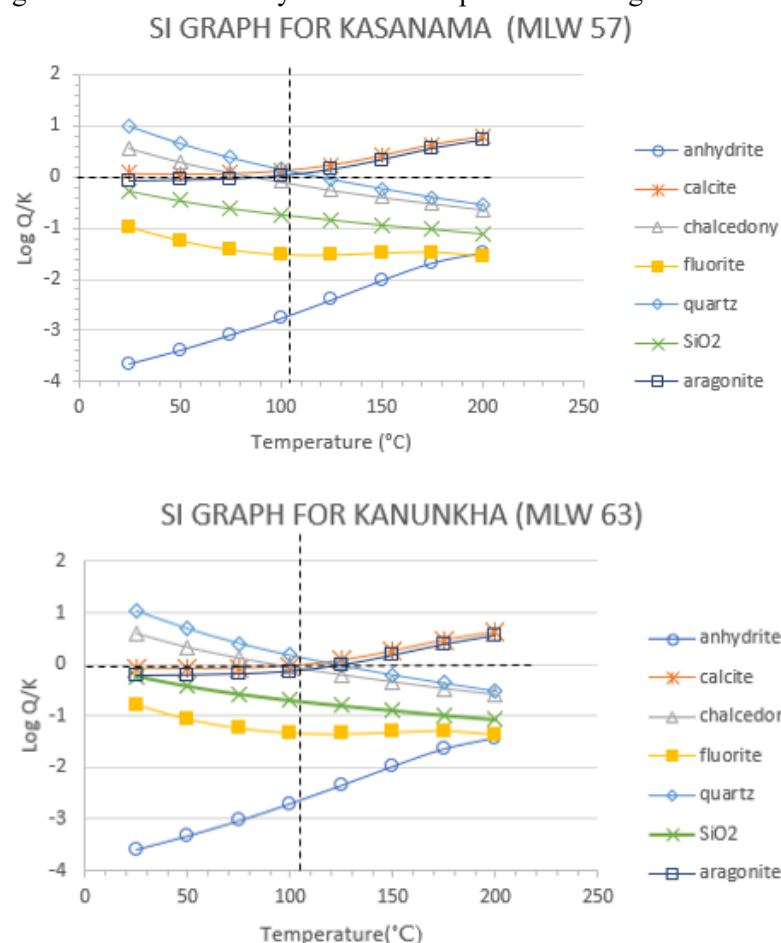
TABLE 1: Geothermometer results of from samples of thermal waters in N-Malawi

(°C)	Chiweta (MLW 51)	Kasitu (MLW 47)	Kasanama (MLW 57)	Kanunkha (MLW 63)
Surface temperature	79	75	60	54
Quartz	132	105	115	78
Na/K	141	91	80	91
Chalcedony	105	75	86	79

The subsurface temperatures of the prospects are all below 180°C which makes the Na/K and quartz geothermometers not very reliable, leaving the chalcedony geothermometer as the most likely candidate for the calculation of subsurface temperature. Looking at the results of the geothermometers, chalcedony geothermometer suggests subsurface temperatures above 100°C for Chiweta geothermal system, Kasitu geothermal system slightly above 70°C, Kasanama with temperature above 80°C and lastly Kanunkha with a temperature of almost 80°C.

Multiple mineral equilibria

The PHREEQC program was used to calculate speciation and saturation index of the minerals. The geochemical data analysis of the samples from the geothermal assessment in Malawi did not include



aluminium, and as a result no Al-containing minerals could be used for calculating saturation indices.

The samples from Kasitu (MLW 47), Chiweta (MLW 51), Kanunkha (MLW 63) and Kasanama (MLW 57) were used in calculating the saturation index. The samples were evaluated chemically and appeared to be good and reliable, based on the ionic charge balance and mass balance. The following minerals were used: anhydrite, calcite, chalcedony, fluorite, quartz, amorphous silica, and aragonite.

Saturation index graphs

Log Q/K graphs were constructed from the saturation index data to obtain the saturation temperatures with several hydrothermal minerals.

Results from the Log Q/K graphs display that samples from Kasanama (MLW 57) (Figure 9)

FIGURE 9: Log Q/K graph for Kasanama and Kanunkha

show few minerals converging at the equilibrium line. This is not surprising since the manifestation is prone to mixing, as some vents are within a swamp region. Therefore, the multiple mineral equilibria graphs are not likely to be of much use. However, the graph agrees with the predictions of geothermometry that chalcedony and the two calcium carbonate phases (calcite and aragonite) converge close to 80°C.

Kanunkha (MLW 63) (Figure 9) also behaves like Kasanama with few minerals converging at the equilibrium line on the Log Q/K graph, but temperatures above 90°C are deduced from the chalcedony and the calcium carbonate minerals.

Kasitu (MLW 47) (Figure 10) prospect which is situated on the shore of Lake Malawi, also depicts mixing of the sampled water as shown on the Na-K-Mg ternary plot. As a result, most minerals do not converge on the equilibrium line on the Log Q/K graph. There is no clear pattern that the minerals portray which makes it impossible to derive the temperature-rock equilibrium between most of the minerals and thermal fluids. Unlike Kasanama, hydrothermal minerals tend not to show any form of coherent behaviour which makes it impossible to obtain more information for Kasitu from these plots.

Log Q/K graph for Chiweta sample (MLW 51) (Figure 10) shows that some minerals intersect the zero-saturation index line but other than that, no clear temperature-rock equilibrium between all the minerals and thermal fluids can be deduced. However, it is apparent that chalcedony and fluorite agree at close to 100°C but the calcium carbonate minerals (calcite and aragonite) show equilibrium at lower temperatures (70°C-80°C). This may be a sign of CO₂ degassing before sample collection. A simulation of boiling and/or CO₂ loss might bring these four fluid-mineral equilibria closer.

As indicated in Table 2, the results from the Log Q/K graphs also indicate that calcite and silica are undersaturated or close to saturation in the geothermal systems of interest, with the exception of Kasitu which shows calcite supersaturation from the sampling temperature downwards. This suggests that deposition of these minerals will not be a problem during production and utilisation from Chiweta, Kasanama and Kanunkha. Another important parameter for utilisation is salinity, and from the data it is clear that thermal water samples in the Northern part of Malawi have low or modest salinity, with the highest chloride content at Chiweta which is 328 mg/l.

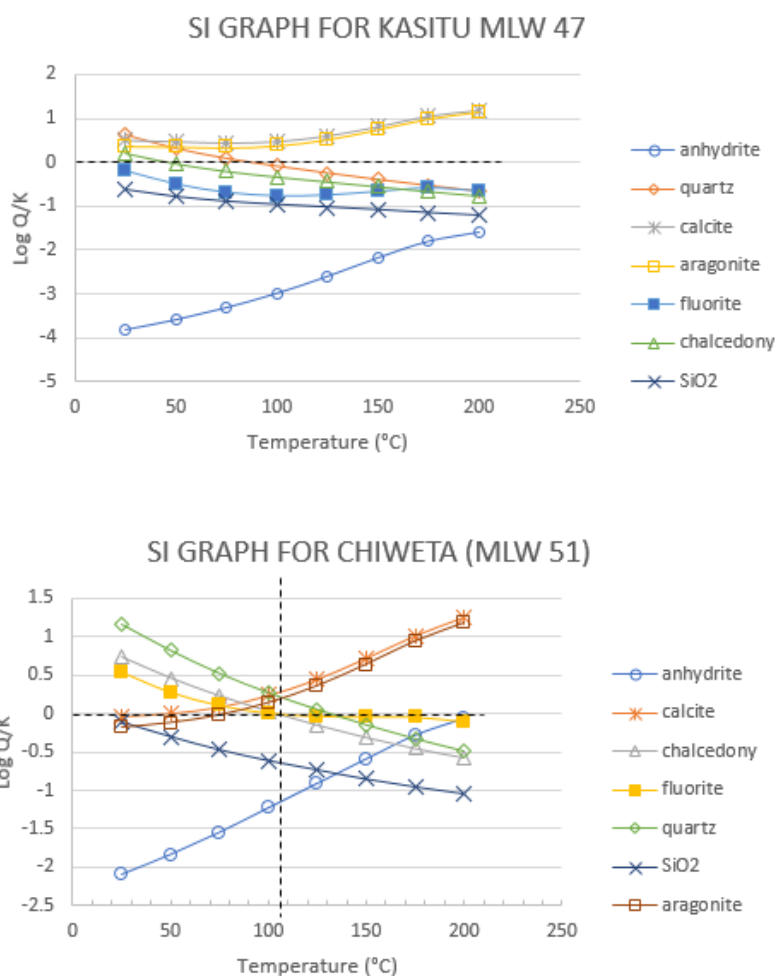


FIGURE 10: Log Q/K graph for Kasitu and Chiweta

TABLE 2: Saturation index for Northern Malawi thermal water samples

Temp (°C)	Kasitu		Chiweta		Kasanama		Kanunkha	
	SiO ₂ (A)	Calcite	SiO ₂ (A)	Calcite	SiO ₂ (A)	Calcite	SiO ₂ (A)	Calcite
25	-0,63	0,51	-0,11	-0,03	-0,27	0,08	-0,24	-0,07
50	-0,79	0,48	-0,30	0,01	-0,46	0,07	-0,43	-0,08
75	-0,90	0,45	-0,47	0,09	-0,61	0,08	-0,58	-0,07
100	-0,97	0,48	-0,61	0,24	-0,73	0,13	-0,70	-0,03
125	-1,03	0,61	-0,73	0,45	-0,83	0,24	-0,80	0,08
150	-1,09	0,82	-0,85	0,72	-0,93	0,42	-0,89	0,26
175	-1,16	1,06	-0,95	1,01	-1,01	0,63	-0,98	0,47
200	-1,22	1,19	-1,04	1,25	-1,10	0,78	-1,06	0,62

5. CONCLUSIONS

Stable isotopes were used to trace the origin of thermal waters and the northern region water samples are meteoric in origin. Since the recharge zone is not Lake Malawi according to the results of the isotope results in Appendix I, the recharge zone is probably on the western side of the hot springs, which is a mountainous region. Elevation of the recharge zone and infiltration are reflected in the depletion of D and ¹⁸O in the geothermal water, compared to local groundwater. There is a slight shift of oxygen for Chiweta samples, approximately 0.5-1‰, probably due to water-rock interaction (oxygen exchange). Kakwewa river, which is at the eastern side of Kasanama is not one of the upflow zones, as was assumed during field work. The Kakwewa river water sample is more enriched than Kasanama water sample, which may suggest that the water recharging the reservoir has fallen as precipitation at a higher altitude.

To classify the thermal waters, Cl-SO₄-HCO₃ and Na-K-Mg ternary plots were used. The thermal waters of the northern part of Malawi are HCO₃ (SO₄) in composition, except for Chiweta water samples, which are Cl (SO₄) in composition. The Cl (SO₄) is assumed to be derived from organic matter since the area is largely overlain by Precambrian basement rocks and Karoo sediments. The Karoo sediments, which are rich in carbonates, also influence the composition of the northern region thermal waters but the connection between rock composition and Cl (SO₄) waters at Chiweta is yet to be identified. Classification of water samples based on equilibrium state depicts that Chiweta samples are equilibrated in terms of cation exchange reactions, unlike Kasanama, Kanunkha and Kasitu, which are only partially equilibrated.

Chalcedony geothermometers suggest subsurface temperatures above 100°C for Chiweta geothermal system, temperatures above 80° for Kasanama and above 70°C for Kasitu and Kanunkha. To supplement the geothermometer subsurface temperature results, multiple mineral equilibria were used. The Log Q/K graphs largely agree with the geothermometers for Chiweta, Kasanama, and Kanunkha but the Log Q/K graph results for Kasitu remains inconclusive.

As indicated in Table 2 the saturation index for calcite and silica of the northern region water samples, all the systems except Kasitu are undersaturated with respect to calcite and amorphous silica, which suggests that these minerals will not precipitate upon production and utilisation. This may be considered a favourable chemical characteristic that will enhance future developments. Chiweta geothermal system has the highest temperature, highest flow rate and the chemical composition is favourable. Further research on Chiweta prospect should be considered.

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APPENDIX I: Isotopic values for thermal water in Northern Malawi (ELC Report)

Code	Name	$\delta^{18}\text{O-H}_2\text{O}$	$\delta^2\text{H-H}_2\text{O}$	d-excess	$\delta^{34}\text{S-SO}_4$
‰ vs. VSMOW	‰	‰ vs. VCDT			
MLW-47	Kasitu-1	-5.75	-34.2	11.8	$+9.45 \pm 0.07$
MLW-48	Kasitu-2	-5.68	-34.3	11.1	$+9.53 \pm 0.02$
MLW-49	Lake Malawi	2.33	14.9	-3.7	-
MLW-50	Kasitu village	-5.3	-31.1	11.3	-
MLW-51	Chiweta-1	-4.1	-24.4	8.3	$+7.79 \pm 0.01$
MLW-52	Chiweta-1B	-4.15	-25.3	7.9	$+7.53 \pm 0.05$
MLW-53	Chiweta-2	-3.94	-24.8	6.8	$+7.93 \pm 0.02$
MLW-54	Chiweta stream	-3.6	-23.7	5.1	-
MLW-57	Kasanama-1	-6.19	-36	13.5	$+9.57 \pm 0.05$
MLW-58	Kasanama-2	-6.07	-34.9	13.7	$+9.33 \pm 0.05$
MLW-63	Kanunkha	-5.9	-34.4	12.8	$+10.37 \pm 0.09$

**APPENDIX II: Results of chemical analysis of northern Malawi water samples
(APPENDIX IV in ELC report, 2016)**

Code	Name	Type	Easting	Northing	Elev.	Outlet T	Flow	pH Fld	T-pH	EC	Eh	Tot Alk Fld	Li	Na	K	Mg	Ca
m	m	m asl	°C	L/s	°C	µS/cm	mV	mg HCO ₃ /L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
MLW-47	Kasitu-1	HS	612184	8642722	479	74.5	0	9.37	34.4	537	-277	161	0.0348	111	3.05	0.05	2
MLW-48	Kasitu-2	HS	612236	8642831	478	76.2	0	9.29	28.8	548	-274	169	0.0347	116	2.8	0.13	1.6
MLW-49	Lake Malawi	LK	612210	8642800	477	25.1	-	8.68	25.1	273	247	151	0.0002	23	6.4	8.3	20.8
MLW-50	Kasitu village	BH	611878	8639539	509	27.2	-	6.59	27.7	409	194	229	0.0391	30	2.07	7	49
MLW-51	Chiweta-1	HS	629670	8818900	495	79.1	Tot >44	8.13	36.7	2080	-321	171	0.333	429	23.7	0.04	20.5
MLW-52	Chiweta-1B	HS	629664	8818900	497	79.2	Tot >44	8.1	33.9	2090	-266	222	0.317	424	22.8	0.02	20.1
MLW-53	Chiweta-2	HS	629722	8818857	494	78.8	Tot >44	8.48	33.6	2050	-310	222	0.301	432	24.6	0.47	20.3
MLW-54	Chiweta stream	HS	629796	8818817	489	64	Tot >44	8.75	34.5	2050	164	177	0.294	435	27.6	0.45	20.3
MLW-57	Kasanama-1	HS	614241	8697774	577	59.5	2.3	9.36	28.5	443	-262	159	0.0067	91.3	2.1	0.1	1.81
MLW-58	Kasanama-2	HS	614162	8697749	580	56	0.3	9.37	29.6	451	191	146	0.0071	92.3	1.81	0.11	1.31
MLW-59	Kakwewa up	RV	611344	8694386	652	24.2	~12700	8.88	24.2	64.4	250	40.7	0.0004	6	1.9	1.59	6.13
MLW-62	Kakwewa down	RV	615704	8698938	560	22.7	~12700	8.98	22.7	85.6	204	46.8	0.0004	7.65	1.8	1.97	7.4
MLW-63	Kanunkha	HS	635873	8718558	541	54.4	<1	9.3	34.5	552	-286	146	0.0229	113	2.51	0.18	1.4

**APPENDIX III: Results of chemical analysis of Northern Malawi water samples
(APPENDIX IV in ELC report, 2016)**

Code	Tot Alk Lab	Non-C Alk	C-Alk1	C-Alk2	SO4	Cl	F	Br	NO3	NH4	SiO2,FA	SiO2,FDA	SiO2,m	B	As	ΣS
mg HCO3/L	mg HCO3/L	mg HCO3/L	mg HCO3/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg HS/L	
MLW-47	157	51.3	106.2	83.3	49.4	10	17.9	0.04	<0.01	0.04	83.2	73.6	78.4	0.03	<0.0001	12.4
MLW-48	157	94	63.5	39.2	51.3	10.2	18	0.05	<0.01	0.06	82.4	73.3	77.9	0.028	<0.0001	13.1
MLW-49	156	-	-	-	4.08	6.97	0.48	0.023	0.025	0.03	1	-	-	0.011	<0.0001	-
MLW-50	232	-	-	-	3.18	11.9	0.81	0.016	0.149	0.02	77	-	-	<0.0005	0.0001	-
MLW-51	164	48.8	114.7	63.1	312	320	13.2	0.635	<0.01	0.33	94.2	90.9	92.5	0.521	0.029	27.9
MLW-52	159	29.3	129.4	42.3	308	323	9.1	0.74	<0.01	0.37	97.5	91	94.3	0.47	0.0298	51.4 ?
MLW-53	172	53.7	118.4	32.1	315	321	13.2	0.618	<0.01	0.32	95.8	94.3	95	0.447	0.0249	46.6
MLW-54	168	68.3	100.1	31.5	319	328	13.3	0.76	0.03	0.13	93	92.2	92.6	0.408	0.0178	37.1
MLW-57	138	43.9	94	73.5	59.7	6.6	6.36	0.02	<0.01	0.07	83.4	93	88.2	0.009	<0.0001	11.1
MLW-58	133	53.7	79.3	59.7	59.9	6.7	6.32	0.02	<0.01	0.03	80.6	80.5	80.5	0.018	0.0001	10.6
MLW-59	37.8	-	-	-	1.3	1.25	0.05	<0.05	0.01	-	25.6	-	-	<0.0005	<0.0001	-
MLW-61	144	90.3	53.7	32	42.7	5.5	4.56	<0.05	1.72	0.05	73.6	78.1	75.9	<0.0005	<0.0001	11.7
MLW-62	45.2	-	-	-	1.5	1.4	0.08	<0.05	<0.01	0.04	27.9	-	-	<0.0005	<0.0001	-
MLW-63	139	51.3	87.9	65.7	95.7	21.1	9.4	0.04	1.2	0.03	96.4	97.3	96.8	0.02	0.0001	12.0 ?