

## Chemical and Isotopic Composition of Thermal Waters in Northern Part of Malawi

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### ABSTRACT

The focus of this study are four geothermal prospects in northern Malawi including Chiweta, Kanunkha, Kasitu and Kasanama which form a linear pattern along Lake Malawi. These prospects have similar geological and structural characteristics. Stable isotopes indicate that thermal waters are meteoric in origin. However, a slight enrichment in  $\delta^{18}\text{O}$  for Chiweta waters may be attributed to relatively more intense water-rock interaction. Karoo sediments influence the  $\text{HCO}_3^-$ -rich composition of the thermal waters. The thermal waters are partially equilibrated with the rock except for Chiweta where discharges are mature geothermal waters. Amongst the four prospects, the Chiweta system has the highest subsurface temperature of  $>100^\circ\text{C}$ . The other prospects have temperatures  $>70^\circ\text{C}$ . Multiple mineral equilibria results agree with projected subsurface temperatures based on the chalcedony geothermometer; they also indicate that calcite and amorphous silica are undersaturated in the systems and thus will not likely cause scaling problems during geothermal production and utilization. Of the four prospects in this study, Chiweta has the most favorable geothermal attributes that warrants more detailed studies.

### 1. INTRODUCTION

Malawi is a landlocked country in south-eastern Africa. It lies between latitudes  $8^\circ\text{S}$  and  $18^\circ\text{S}$ . Although the country has not been subjected to recent volcanism, it is endowed with non-volcanic geothermal resources (Gondwe et al., 2015).

Malawi is underlain by crystalline Precambrian to lower Paleozoic high-grade metamorphic rocks and igneous rocks in the highlands and plateau areas. 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 alluvial and lacustrine sediments. In the northern part of the country, a correlation has been made between the Neogene tuffs inside the northern border of Malawi and Tanzania and 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 and consists of a series of half grabens which 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 where you find the Urema graben and the Dombe trough in Mozambique. Most of the important younger structures, which are significant in the search for geothermal systems, are products of Precambrian ductile deformation. Lake Malawi has three linked half graben basins: Karonga, Nkhatabay and Nkhosha. These are largely controlled by a major bounding faulting system. In the southern part of the country, tectonic features portray a NW-SE trend similar to the northern part (ELC, 2016).

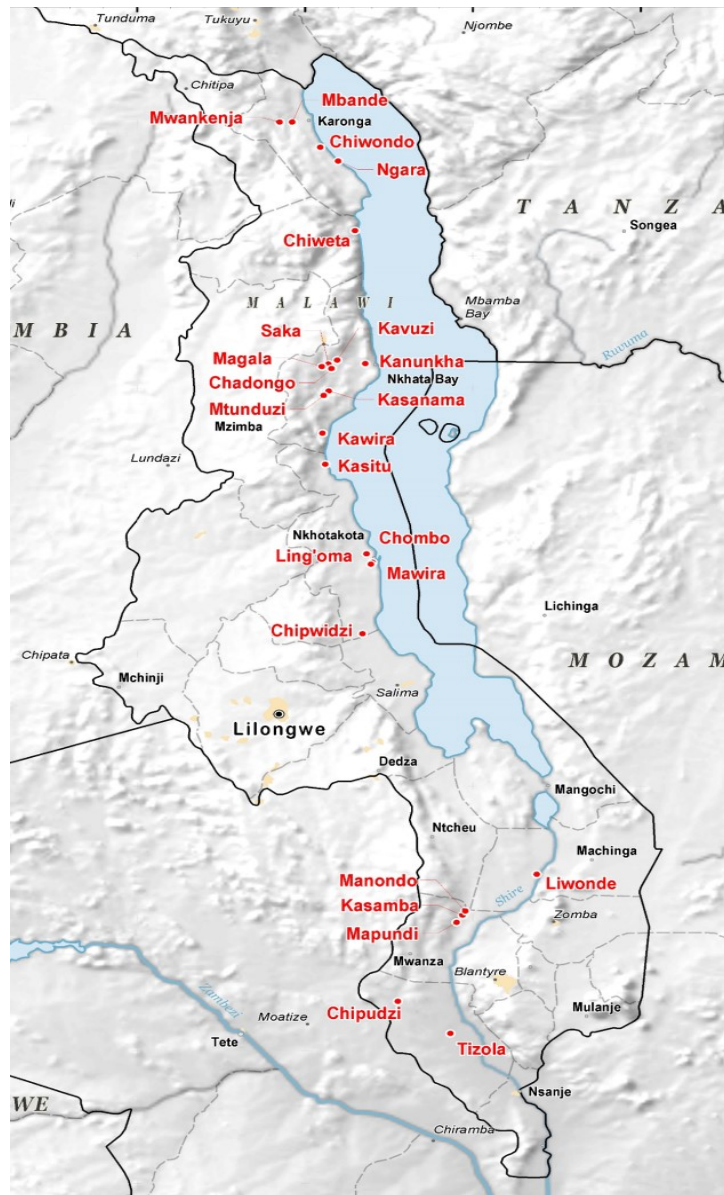
### 2. GEOTHERMAL RESOURCE INVESTIGATIONS IN MALAWI

Several geochemical studies have been carried out throughout the country to obtain an overall picture of geothermal manifestations in the country. Initial studies by the Geological Survey of Malawi in 2003 reexamined available information from the 1990s to assess the suitability of geothermal resources for power generation. Geochemical studies from that time were not comprehensive and more thorough research is recommended (Dulanya, 2006). A reconnaissance survey (geochemical survey) of the manifestations in 2010 by the Geothermal Development Company (GDC) of Kenya suggested that temperatures above  $100^\circ\text{C}$  were the highest temperatures in the northern part of Malawi. GDC recommended that the government of Malawi carry out detailed surface investigations of the prospect areas (GDC, 2010).

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

#### 2.1 First Detailed Assessment of the Geothermal Resources in Malawi

Detailed assessment of geothermal resources from 2016-2017 were carried out by a team from Electroconsult (ELC) in Italy and local personnel from the Ministry of Natural Resources Energy and Mining. The reconnaissance study identified around 50 geothermal manifestations which were grouped into twenty-four prospects with respect to topographic proximity (Figure 1).



**Figure 1: Geothermal manifestations (red dots) in Malawi (Figure 5 in ELC, 2016).**

The manifestations in Malawi are hot springs with surface temperatures as high as 79°C to 84°C.

Detailed geochemical sampling (preliminary appraisal) were subsequently carried out in six prospects in 2016 at Chiweta, Kanunkha, Kasanama, Kasitu, Mawira, Chipudzi, and several borehole samples in Kasungu. These prospects were chosen based on technical and non-technical parameters such as maximum temperature, maximum flow rate, temperature loss, 18-oxygen shift, predicted reservoir temperature, structural and hydrological setting and stratigraphy (ELC, 2016).

Among the six prospects, only Kasanama, Kasitu, Chiweta and Kanunkha in the northern region are used in this study to: (1) trace the origin of the thermal fluids, (2) estimate the temperature and utilization potential of the fluids and (3) look for favourable chemical characteristics that enhance future development.

## 2.2 Geology of the Northern Malawi Geothermal Prospects

The geothermal prospects in the northern region have similar rock types with minor differences in the geological make-up.

The Chiweta prospect (Figure 2) is located in the Rumphi district west of Lake Malawi. The area is overlain by basement complex rocks including biotite gneiss, hornblende gneiss and amphibolites. These are mostly south-west trending and cut by NW-SE and NE-SW faults. The area is also covered by the Karoo sedimentary rocks that outcrop in a basin. The three major units of Karoo include intermediate beds, yellow mudstones, calcareous siltstones and Chiweta beds.

The Kanunkha prospect is situated in the Nkhatabay district (Figure 3) where the largest number of thermal manifestations occur. This prospect is dominated by a large ridge of the Kondoli mountain chain. The foot wall of the ridge is comprised of recent alluvial deposits and thick strata 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.

The Kasanama prospect consists of thermal manifestations found in four localities in the Nkhatabay district referred to as Kasanama 1, Kasanama 2, Kasanama 3 and Mtunduzi. All manifestations occur along a 5 km stretch of the Kakwewa river, which is 25 km west of Lake Malawi (Figure 4). The upper valley of the Kakwewa river is overlain by sedimentary rocks. A conglomeritic facies rich in quartz pebbles is part of the Timbiri beds. Basement complex rocks like biotite gneiss and quartz feldspar gneiss also underlie the area. The flat lowlands of the area are covered by recent alluvial deposits and a thick lateritic soil cover. Mica-rich phyllonites are locally intercalated with the biotite gneiss.

The Kasitu prospect in the Nkhatakota district has two manifestations that emerge on the shore of Lake Malawi (Figure 5). The manifestations form ponds on the shore of the lake which is overlain by alluvial and lacustrine deposits as well as colluvial and residual deposits. Basement complex rocks in the area consist of biotite gneiss.

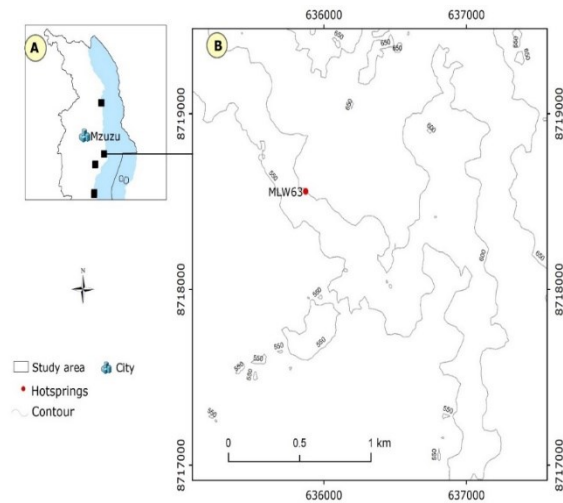


Figure 3: Kanunkha hot springs (MLW 63)

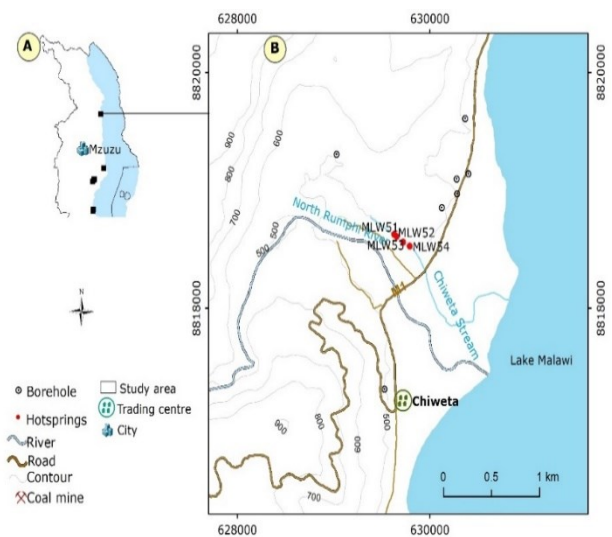


Figure 2: Chiweta hot springs (MLW 51)

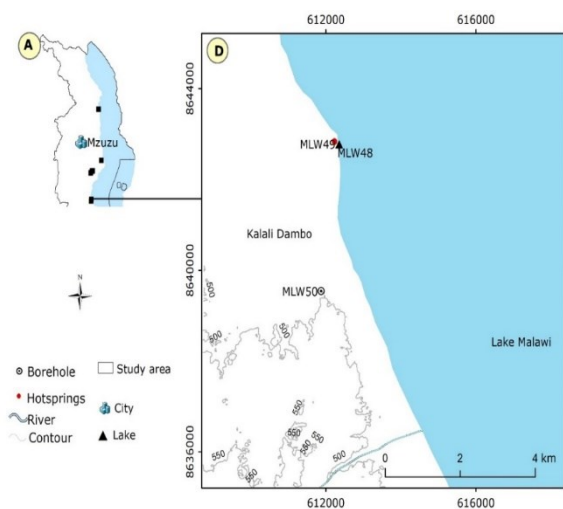


Figure 5: Kasitu prospect (MLW 48,49)

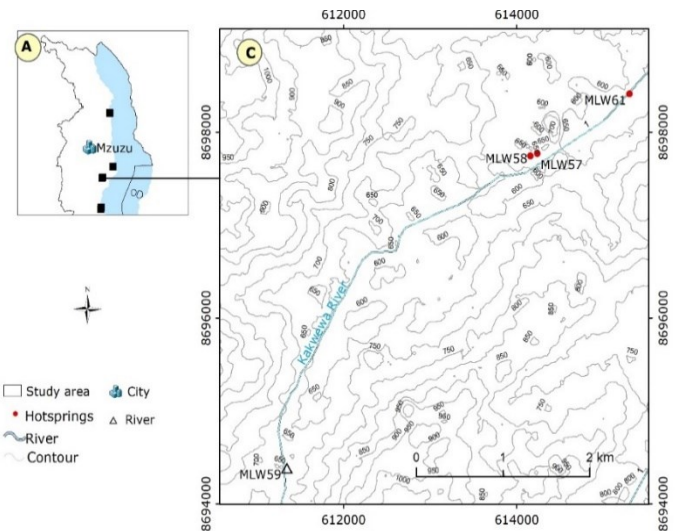


Figure 4: Kasanama prospect (MLW 57,58,61)

### 3. METHODOLOGY

In the course of the preliminary appraisal (ELC, 2016), 31 rock samples for petrographic analysis and 33 water samples from boreholes with thermal water, rivers and Lake Malawi were collected for chemical and isotopic analyses in the laboratory. This data is needed in order to understand the origin of thermal waters associated with the geothermal prospects. Rivers close to some geothermal prospects and Lake Malawi were also sampled to see if there was a link between their parent sources. During the preliminary appraisal, emphasis was put on geochemical sampling of the six prospects as well as detailed geological mapping. As part of the geochemical study, the following on-site measurements were made: temperature measurements using a thermocouple, total alkalinity by acidimetric titration, flow rate measurements and Eh, pH and electrical conductivity using a portable multi-parametric device.

The samples were preserved using appropriate treatments such as filtration, acidification, dilution, and precipitation. Membrane filters with a pore size of 0.45  $\mu\text{m}$  were used to remove particulate matter. Pure  $\text{HNO}_3$  and  $\text{HCl}$  were added to the appropriate samples to preserve cations and dissolved metals and resist precipitation and oxidation. To avoid silica precipitation and polymerization, dilution and acidification processes were used. Chemical and isotopic analysis of the water samples was conducted in Italy and the United Kingdom.

### 4. RESULTS AND DISCUSSION

#### 4.1 Origin and Classification of Thermal Waters in the Northern Part of Malawi

##### 4.1.1 Stable isotopes

Most of the data from water samples in the northern region lies close to the global meteoric water line (Craig, 1961; Figure 7). The only sample data that does not fall on the line is from the Chiweta hot springs which show a slight 18-oxygen shift of approximately 0.5-1‰. This is probably due to oxygen exchange with the host rock. From Figure 7, 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 as indicated by the more enriched isotopic values for the lake water (+2.33 for  $\delta^{18}\text{O}$  and +14.9 for  $\delta^2\text{H}$ ) relative to the isotopic values of the thermal water samples. However, it is possible that the Kasanama, Kanunkha and Kasitu prospects are fed by the same or a similar source.

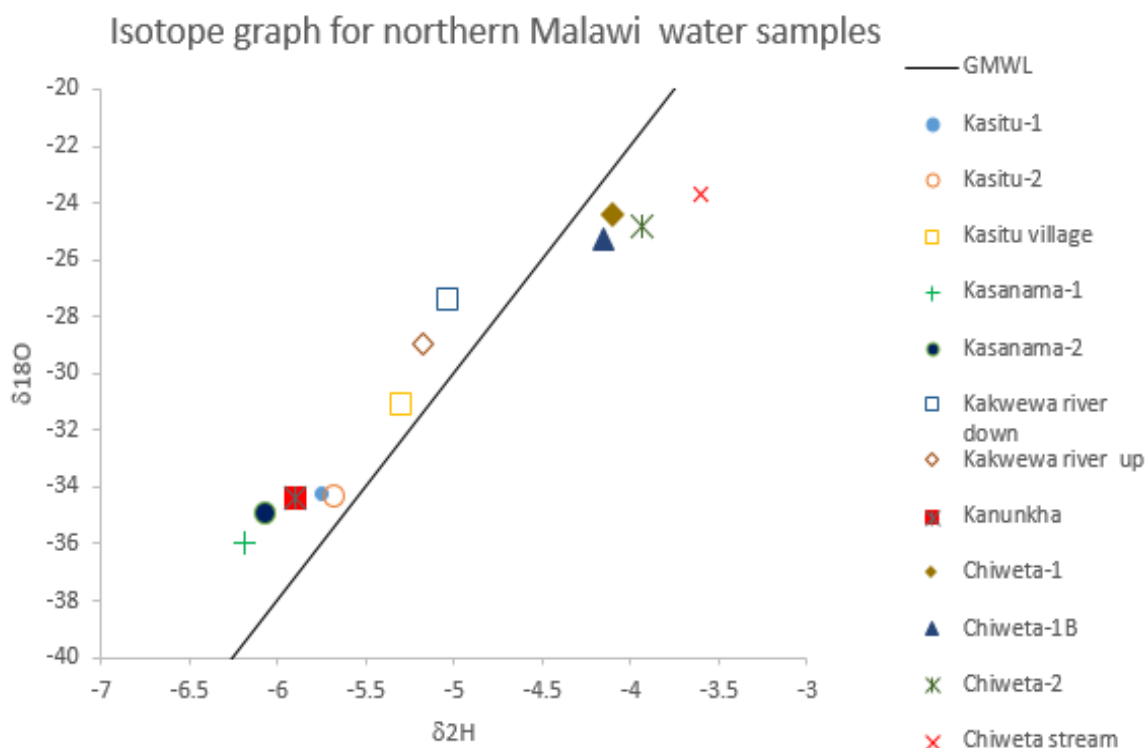


Figure 7:  $\text{d}^2\text{H}$  vs  $\text{d}^{18}\text{O}$  graph for northern Malawi samples

From the previous report published by the Electro-consult (ELC, 2016), all the Kasanama manifestations are located on the eastern side of Kakwewa river and are following a NE-SW fault. This leads to the assumption that the Kakwewa river might be a major source of recharge for the Kasanama hot springs. However, the isotopic plot shows that samples from the Kasanama and Kanunkha hot springs are depleted in deuterium relative to the Kakwewa River; this suggests recharge from a higher altitude than the Kakwewa River and from precipitation in the mountainous region west of the hot springs. Similarly, the Kasitu hot springs must have a different origin than the water collected at Kasitu village (borehole).

#### 4.1.2 Cl-SO<sub>4</sub>-HCO<sub>3</sub> triangular diagram

Most manifestations in Malawi discharge HCO<sub>3</sub>-rich waters (Figure 8). These waters are often products of fluid mixing or steam and gas condensation and are commonly known as peripheral waters. The Kanunkha, Kasitu and Kasanama prospects discharge HCO<sub>3</sub>-rich waters with Cl- SO<sub>4</sub> rich waters sampled from the Chiweta hot springs. Most of the prospects in the northern region are associated with the Karoo sedimentary rocks which have carbonate-rich strata that contribute to the high carbonate content of most thermal waters discharging along the lake.

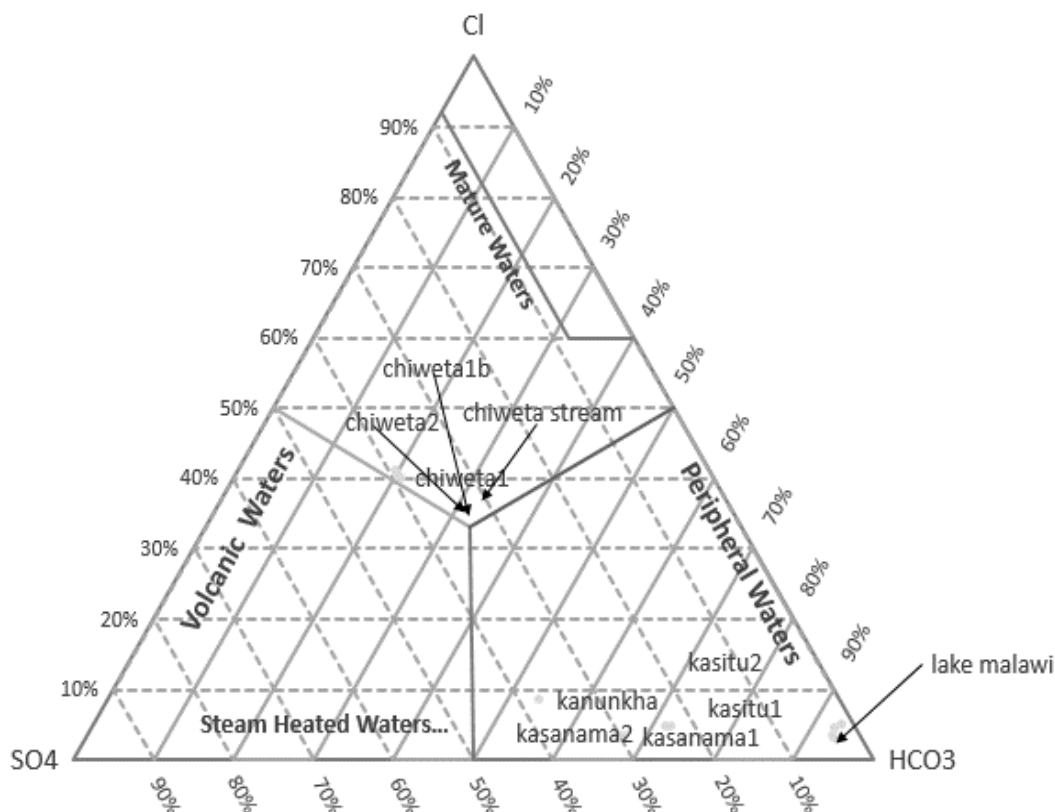


Figure 8: Cl-SO<sub>4</sub>-HCO<sub>3</sub> ternary plot for northern Malawi samples

#### 4.1.3 Na-K-Mg triangular diagram

As illustrated in the Na-K-Mg ternary plot (Figure 9), most of the waters at Kasitu, Kasanama, and Kanunkha are partially equilibrated at similar temperatures deeper in the crust. The waters may have been mixed with magnesium-rich meteoric waters along the way to the surface. Only Chiweta 1b waters fall on the full-equilibrium line with two plotting on the partially equilibrated region. This suggests that the Chiweta thermal water is more mature and/or less mixed than aqueous fluids from Kasitu, Kasanama and Kanunkha. All the samples collected from the rivers, lake, and boreholes in some of the areas close to the sampled areas are considered immature as they fall on the meteoric water line due to interaction with surface water.

Table 1 shows estimated subsurface temperatures based on the Na/K (Arnórsson et al., 1983), quartz (Fournier and Potter, 1982) and chalcedony (Fournier, 1977) geothermometers.

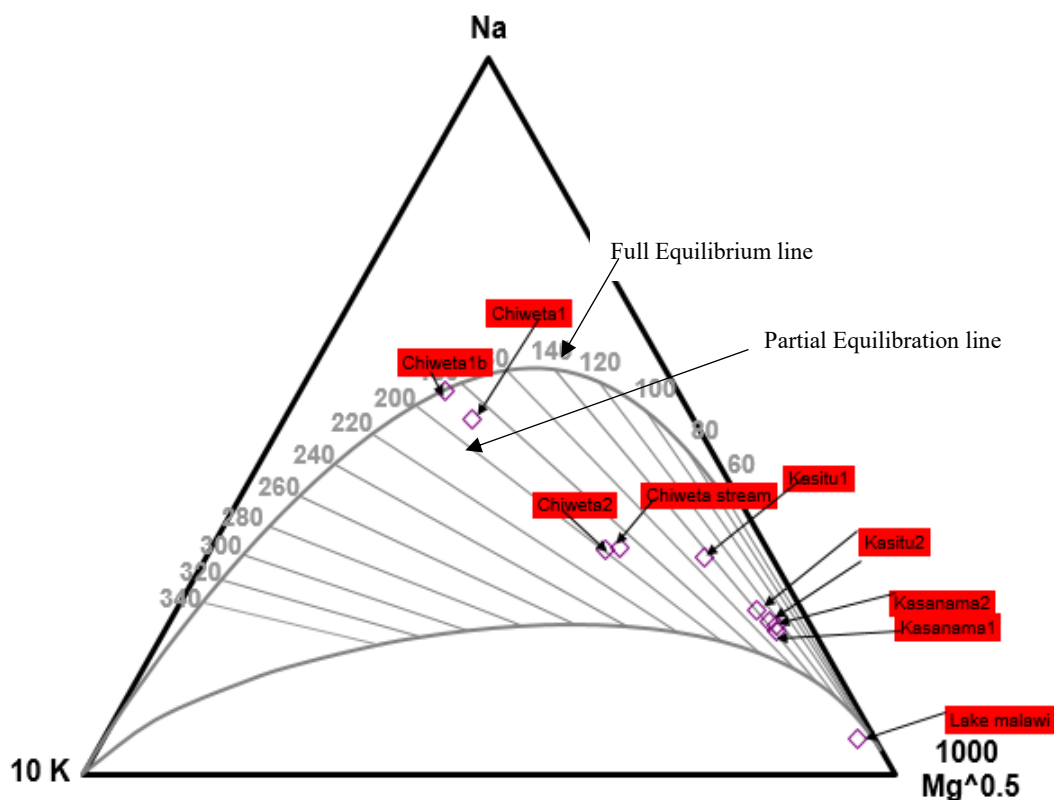


Figure 9: Na-K-Mg ternary plot for northern Malawi water samples

TABLE 1: Geothermometer results of thermal waters in northern Malawi

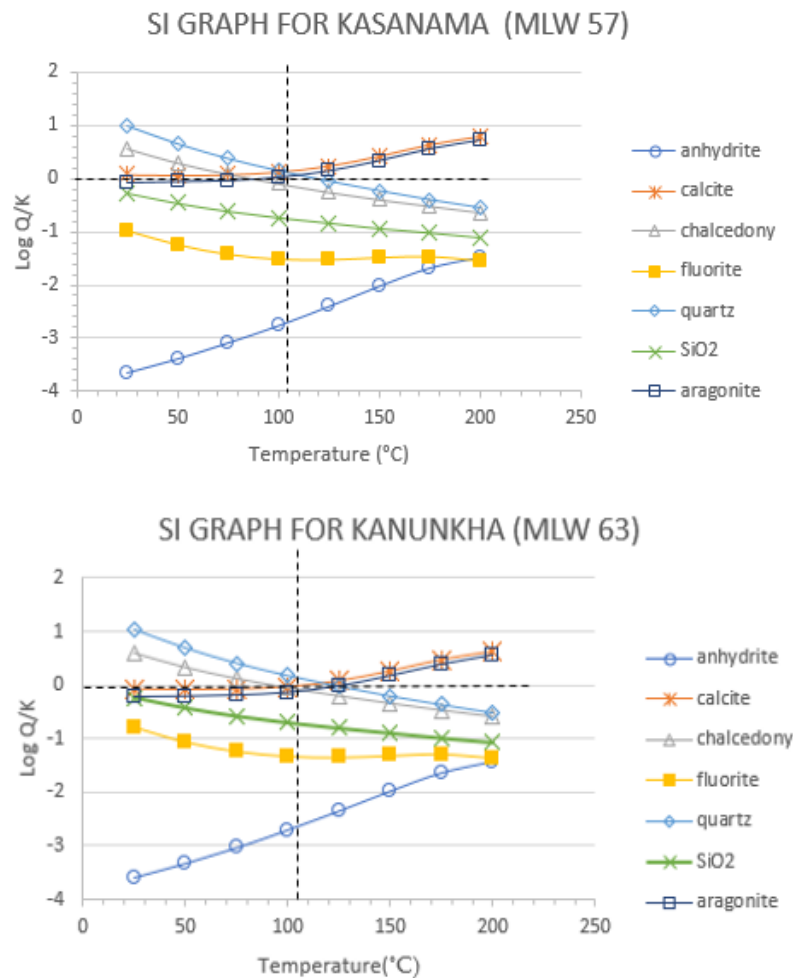
SAMPLE				
(°C)	Chiweta (MLW 51)	Kasitu (MLW 47)	Kasanama (MLW 57)	Kanunkha (MLW 63)
Surface Temperature	79	75	60	54
Quartz	132	105	115	78
Na/K	141	91	80	91
Chalcedony	105	75	86	79

From the previous findings of Electroconsult and GDC, the subsurface temperatures of the prospects are all below 180°C which makes the Na/K and quartz geothermometers not suitable. This leaves the chalcedony geothermometer as the most likely candidate for the calculation of subsurface temperature. Thus, the 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.

#### 4.1.4 Multiple-component mineral equilibria

The PHREEQC program (Parkhurst and Apello, 2013) was used to calculate the speciation and saturation indices of minerals. Because Al was not analyzed in the water samples, no saturation indices for Al-containing minerals could be calculated. Instead, the following minerals were selected: anhydrite, calcite, chalcedony, fluorite, quartz, amorphous silica, and aragonite.

For the saturation index calculations, samples from Kasitu (MLW 47), Chiweta (MLW 51), Kanunkha (MLW 63) and Kasanama (MLW 57) were selected based on the reliability of the chemical analyses deduced from the ionic charge balance and mass balance.



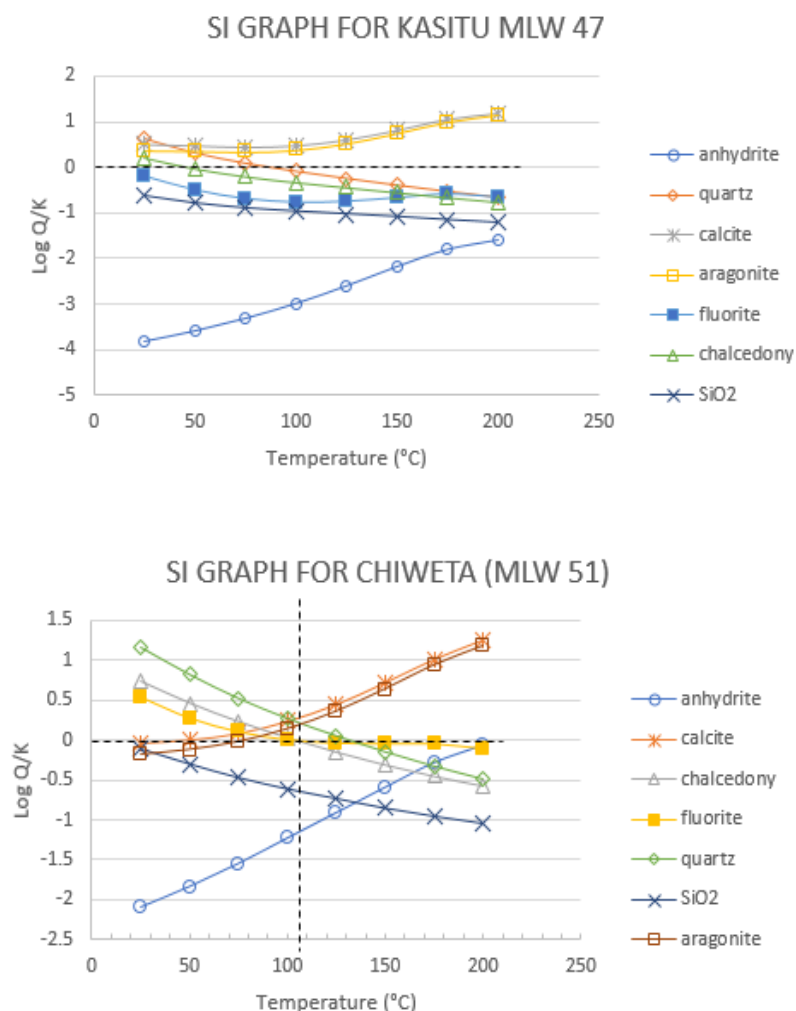
**Figure 10: Log Q/K graph for Kasanama and Kanunkha**

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

Results from the Log Q/K graphs show that samples from Kasanama (MLW 57) (Figure 9) have 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. The graph concurs with the predictions of geothermometry that chalcedony and the two calcium carbonate phases (calcite and aragonite) converge at about 80°C on the zero saturation index line agreeing with chalcedony geothermometry (Table 1). Similarly, chalcedony and the calcium carbonate minerals in the Kanunkha (MLW 63) (Figure 10) sample converge, albeit at >90°C.

The Kasitu (MLW 47) (Figure 11) prospect is situated on the shore of Lake Malawi and, like the other three prospects in this study, shows mixing with meteoric water. However, unlike Kasanama and Kanunkha, the hydrothermal minerals show no clear convergence.





**Figure 11: Log Q/K graph for Kasitu and Chiweta**

The log Q/K graph for Chiweta sample (MLW 51) (Figure 11) shows that some minerals intersect the zero-saturation index line. However, it is apparent that chalcedony and fluorite converge at nearly 100°C but the calcium carbonate minerals (calcite and aragonite) show equilibrium at lower temperatures (70°C-80°C). This may be indicative of CO<sub>2</sub> degassing before sample collection. A simulation of boiling and/or CO<sub>2</sub> loss may bring these four fluid-mineral equilibria closer.

Log Q/K graphs (Table 2) indicate that calcite and silica are undersaturated in the geothermal systems of interest, except 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 utilization in Chiweta, Kasanama and Kanunkha. Another important parameter for utilization is salinity. Based on the data collected during the first detailed assessment of Geothermal prospects in Malawi, it is clear that thermal water samples in the northern part of Malawi have low or modest salinity with the highest chloride content of 328 mg/l at Chiweta.

**Table 2: Saturation index for Northern Malawi thermal water samples**

	Kasitu		Chiweta		Kasanama		Kanunkha	
TEMP	SiO <sub>2</sub> (A)	CALCITE	SiO <sub>2</sub> (A)	CALCITE	SiO <sub>2</sub> (A)	CALCITE	SiO <sub>2</sub> (A)	CALCITE
25	-0.63	0.51	-0.11	-0.03	-0.27	0.08	-0.24	-0.07
50	-0.79	0.48	-0.3	0.01	-0.46	0.07	-0.43	-0.08
75	-0.9	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	-0.7	-0.03
125	-1.03	0.61	-0.73	0.45	-0.83	0.24	-0.8	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	-1.1	0.78	-1.06	0.62



## CONCLUSIONS

Stable isotopes indicate that thermal waters and the northern region water samples are meteoric in origin. The recharge zone is not Lake Malawi but probably the mountainous region on the western side of the hot springs. Elevation of the recharge zone and infiltration are reflected in the depletion of D and  $^{18}\text{O}$  in the geothermal water relative to the local groundwater. There is a slight shift in 18-oxygen for Chiweta samples; approximately 0.5-1‰ most likely due to the water-rock interaction (18-oxygen exchange). Kakwewa river, located on the eastern side of Kasanama, is not a source of recharge. The Kakwewa river water sample is more enriched than the Kasanama water sample, which may suggest that the water recharging the reservoir has fallen as precipitation at higher altitudes.

The thermal waters of the northern part of Malawi are  $\text{HCO}_3$  in composition, except for Chiweta water samples which are  $\text{Cl-SO}_4$  in composition. The  $\text{HCO}_3$  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  $\text{Cl-SO}_4$  waters at Chiweta is yet to be identified. Thermal waters discharged at 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  $>100^\circ\text{C}$  for Chiweta geothermal system,  $>80^\circ$  for Kasanama and  $>70^\circ\text{C}$  for Kasitu and Kanunkha. To supplement the geothermometer subsurface temperature results, multiple mineral equilibria were used. The log Q/K graphs agree well with the geothermometers for Chiweta, Kasanama, and Kanunkha but are inconclusive for Kasitu.

Thermal water discharges in the studied geothermal prospects, except Kasitu, are undersaturated with respect to calcite and amorphous silica. This indicated that these minerals will not precipitate upon production and utilization. This could be considered a favourable chemical characteristic that will enhance future development. The Chiweta geothermal system has the highest temperature, highest flow rate and has the most favourable chemical composition among the four prospects. Hence, further research on Chiweta prospect should be considered.

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