

Full Length Research Paper

Spatial distribution, chemistry and subsurface temperatures of geothermal springs in Nkhata bay, Malawi

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Received 24 March, 2014; Accepted 1 August, 2014

This study investigated the spatial distribution, chemistry and subsurface temperatures of geothermal springs in Nkhata Bay, Malawi, which lies in the Western Branch of the East African Rift System. Seventeen geothermal springs were identified and mapped in the District. Eleven of these geothermal springs were purposively sampled for chemistry study on the basis of their spatial distribution representativeness and accessibility for reassessment. Two water types were hydrochemically delineated: sodium-sulfate (Na-SO_4) and sodium-sulfate-bicarbonate ($\text{Na-SO}_4\text{-HCO}_3$). Additionally, several mineral species were inferred to have been in contact with the geothermal spring waters in the district: calcite, aragonite, dolomite, gypsum, anhydrite, halite, fluorite, goethite, siderite and haematite. The thermal spring waters were undersaturated with respect to aragonite, calcite, dolomite, gypsum, anhydrite, halite and fluorite. However, four geothermal springs were supersaturated with respect to goethite, haematite and siderite. Although all the geothermal springs were undersaturated with fluorite (CaF_2), all contained higher F^- concentrations (from 2.21 ± 0.06 to 10.27 ± 0.25 mg/L) than the World Health Organization (WHO) recommended limit for drinking water (1.5 mg/L). This suggests that fluoride does not precipitate as CaF_2 in the springs but mobilizes freely in the thermal waters without forming other complexes. The cadmium levels in four thermal springs exceeded the Malawi Bureau of Standards (MBS) and WHO safe limit for human consumption (0.005 mg/L). Furthermore, the iron levels in three springs exceeded the WHO and MBS safe limit (0.20 mg/L). Evidently, the chemistry of geothermal springs in Nkhata Bay shows that their utilization for drinking is not suitable. The Giggenbach Triangle revealed that all but one of the springs had fully equilibrated waters. Hence, chemical geothermometers were used to estimate their original subsurface temperatures. Information about these temperatures is required for the assessment of possible geothermal power stations. Amongst the geothermometers used, the Na/K/Ca and Na/K geothermometers offered better and more robust estimates ($P > 0.01$) of geothermal subsurface temperatures. These geothermometers indicated that the original subsurface temperatures were in the ranges of 85 - 209 and 112 - 280°C, respectively.

Key words: Geothermal springs, spatial distribution, chemistry, subsurface temperatures.

INTRODUCTION

Most geothermal springs in the world occur in rift systems, more particularly, in areas along the tectonic

plate boundaries where magma tends to rise towards the earth's surface (GEO, 2007). Malawi, which lies in the

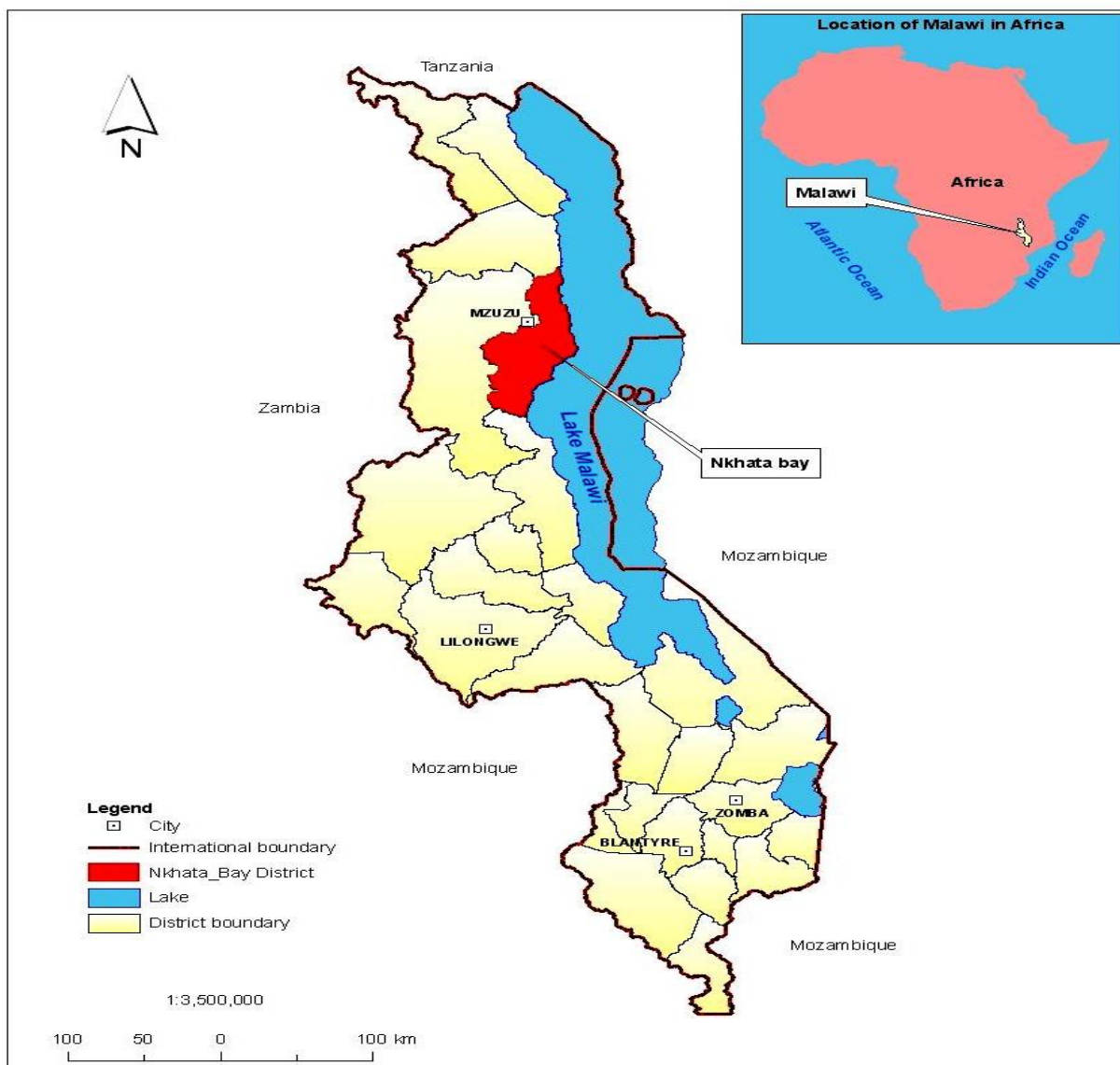


Figure 1. Location of Nkhata Bay, Malawi.

Western Branch of the East African Rift System, has thus many geothermal springs across the country from north to south (Dulanya, 2006).

The presence and distribution of geothermal springs in some parts of Malawi such as Chitipa, Karonga, Rumpi, Nkhotakota, Machinga, Mulanje, Zomba and Chikwawa Districts have been documented and their chemistry described by Harrison and Chapusa (1975), Ray (1975), Kalindekafe (2003) and Dulanya (2006), among others. Nkhata Bay located in the rift-valley floor in the north-eastern part of the country, along Lake Malawi (Figure 1),

has numerous geothermal springs but lack research details of their spatial (Appendix 1) distribution and chemistry.

This study was therefore undertaken to investigate the spatial distribution, chemistry and subsurface temperatures of geothermal springs in Nkhata Bay, Malawi, recognizing the important roles similar geothermal resources play in many different parts of the world including boosting tourism in the country, mineral extraction, balneology and production of geothermal electricity.

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MATERIALS AND METHODS

Locations of geothermal springs

Geothermal springs were identified in Nkhata Bay using indigenous information. The Universal Transverse Mercator (UTM) coordinates of the thermal springs were recorded using Global Positioning System (GPS) receiver. These UTM coordinates were superimposed on the electronic (scanned) map of Nkhata Bay obtained from Malawi National spatial Data Center, geo-referenced and digitized in the ArcView 3.3 Software.

Thermal springs chemistry

Water sampling

Eleven thermal springs were purposively sampled in order to study their chemistry. Sampling was done in December, 2007. Grab sampling was used in collecting water samples from geothermal spring-heads. Samples were collected in triplicates using 2 L polyethylene bottles and labelled accordingly. Samples meant for metal or cation analyses were acidified on the spot with concentrated nitric acid (1.5 mL HNO₃ per litre of collected water samples) according to APHA (1989).

Analytical procedures

Physico-chemical and chemical parameters

The physico-chemical parameters such as temperature, pH and electrical conductivity were measured in the field and chemical parameters, Na, K, Ca, Mg, Fe, Al, Cd, SiO₂, Pb, Cr, F⁻, Cl⁻, NO₃⁻, PO₄³⁻, HCO₃⁻ and SO₄²⁻, were determined in the laboratory according to APHA (1989).

1. Quantitative analysis of physico-chemical and chemical parameters

Determination of electrical conductivity (EC): The electrical conductivity of water samples was determined in the field using WPA - CM 35 conductivity meter. The electrode of the meter was rinsed before dipping into subsequent water samples to prevent inter-sample contamination (APHA, 1989).

Determination of temperature: A silver thermometer (graduated up to 300°C) was used to determine temperature at the spring-heads of the geothermal springs *in situ*. The thermometer was immersed in the thermal water and readings were taken on the spot according to APHA (1989).

Determination of pH: The pH of water samples was determined in the field at sampling points using a glass electrode Kent EIL 7020 pH meter. Prior to the pH determination, the meter was calibrated using pH 7 and 4 buffering solutions, respectively. The meter's electrode was rinsed with distilled water before determining the pH of any subsequent sample to prevent inter-sample contamination (APHA, 1989).

2. Analysis of metals/cations

The nitric acid digestion method was used for metal/cation determination (APHA, 1989). A well-homogenized unfiltered sample (100 ml) was transferred to a 250 ml flask and 5 ml of concentrated

nitric acid was added to it. The mixture was then brought to slow boiling and evaporated on a hot plate until the volume was reduced to 15-20 ml. Concentrated nitric acid (5 ml) was added to the solution and the flask covered with a watch glass before heating it to obtain a gentle refluxing. The heating continued whilst adding 5 ml portion of nitric acid until the solution became light coloured clear solution.

Finally, concentrated nitric acid (2 ml) was added to dissolve any remaining residues and later the solution was quantitatively filtered into 100 ml volumetric flask and diluted to the mark (APHA, 1989). The preparation of standard solutions for analysis of metals in water samples were done briefly as follows: For each of the metals, an aliquot of 10 mL taken from 1000 ppm standard stock solution were diluted with distilled water in a 100 mL volumetric flask to prepare an intermediate stock solution (100 ppm). Then, appropriate volumes of the intermediate stock solutions (0.0, 2.0, 4.0, 6.0, 8.0, 10.0, and 20 mL) were diluted with distilled water in 100 mL volumetric flasks to prepare working standard solutions of 0.0, 2.0, 4.0, 6.0, 8.0, 10.0 and 20.0 ppm, respectively. Absorbances of working standard solutions and water samples were determined using Atomic Absorption Spectrophotometer (AAS), Buck Scientific model no. 200A.

Cadmium (Cd): A standard stock solution (1000 ppm) was prepared by dissolving cadmium metal (1.00g) in concentrated nitric acid (4ml) before diluting the resultant solution with distilled water in a 1-L volumetric flask. Absorbances of the working standard solutions and samples were read at 228.8 nm (APHA, 1989).

Chromium (Cr): A standard stock solution (1000 ppm) was prepared by dissolving anhydrous potassium dichromate (2.83 g) in distilled water (200mL). Concentrated nitric acid (2 mL) was added to the solution before diluting with distilled water in a 1-L volumetric flask. Absorbances of the working standard solutions and samples were read at 357.9 nm (APHA, 1989).

Lead (Pb): A standard stock solution (1000 ppm) was prepared by dissolving lead nitrate (1.60 g) in distilled water (200 mL). Concentrated nitric acid (2 mL) was added to the solution before diluting with deionised water in a 1-Litre volumetric flask. Absorbances of the working standard solutions and samples were obtained at 283.3 nm (APHA, 1989).

Iron (Fe): A standard stock solution (1000 ppm) was prepared by dissolving iron wire (1.00 g) in 1+1 nitric acid water (50 mL). The standard solutions used in the final determination were 0.00, 0.5, 1.0, 2.0, 5.0 and 10.0 ppm. Absorbance of the working standard solutions and samples were read at 248.3 nm (APHA, 1989).

Sodium (Na): A standard stock solution (1000 mg/L) was prepared by dissolving sodium chloride (2.542 g) in 1 L volumetric flask and diluted to volume with the distilled water. The standard solutions used in the final determination were 0.0, 2.0, 4.0, 6.0, 8.0, 10.0, and 20 mg/L. Absorbances of the working standard solutions and samples were read at 589.0 nm (APHA, 1989).

Potassium (K): A standard stock solution (1000 ppm) was prepared by dissolving potassium chloride (1.907 g) dried at 110°C and later diluted to 1 L with distilled water. The standard solutions used in the final determination were 0.00, 0.5, 1.0, 2.0, 5.0 and 10.0 ppm. Absorbances of the working standard solutions and samples were read at 769.9 nm (APHA, 1989).

Calcium (Ca): The standard calcium (Ca) stock solution (1000 mg/L) was prepared by adding distilled water (50 mL) to calcium carbonate, CaCO₃, (2.497 g) and adding drop-wise concentrated hydrochloric acid, HCl, (10 mL) to complete dissolution. The solution was subsequently diluted to the mark in 1000-ml volumetric

flask. The stock solution was used to prepare an intermediate stock solution (100 mg/L) from which the working standard solutions were prepared. The standard solutions used in the final determination were 0.00, 0.5, 1.0, 2.0, 5.0 and 10.0 mg/L. Absorbances of the standard solutions and samples were read at 422.7 nm on the AAS (APHA, 1989).

Determination of magnesium (Mg): A standard stock solution of Mg was prepared as follows: 1.000 g of magnesium ribbon was dissolved in a minimum volume (5 mL) of (1+1) HCl. The solution was diluted to 1 L with 1% (v/v) HCl. The stock solution was used to prepare an intermediate stock solution (100 mg/L) from which the working standard solutions were prepared. The standard solutions used in the final determination were 0.00, 0.5, 1.0, 2.0, 5.0 and 10.0 mg/L. Absorbances of the working standard solutions and samples were read at 285.2 nm on the AAS (APHA, 1989).

Analysis of aluminum (Al): Aluminum concentrations in geothermal spring water samples were determined colorimetrically using UV-VIS spectrophotometer (APHA, 1989). Samples (2 mL each) and aluminum (Al) standards (10 mL each) were separately pipetted into 100-mL flasks. The following were added into each of the standards and samples: 1+199 thioglycolic acid (10 mL) (prepared from 5 mL of the acid diluted to 1000 mL), solochrome cynine solution (10 mL, 0.075%) and ammonium acetate solution (pH 6). Solochrome cynine solution (0.075%) was prepared as follows: solochrome cynine analar (0.75 g) was dissolved in 200 mL of deionised water; sodium chloride (25 g), ammonium nitrate (25 g) and concentrated nitric acid (2 mL) were added into the solochrome cynine solution. This solution was then filtered through 542 Whatman paper (without washing) and was left to stand for overnight before use. Ammonium acetate solution (pH6) was prepared as follows: acetic acid (570 mL) was mixed with distilled water (1130 mL); then ammonium solution (570 mL) was carefully added; the resultant solution was mixed, cooled and adjusted to pH 6 with ammonia using a pH meter. The samples and the standards were topped to the 100-ml mark with distilled water. The aluminum (Al) standards were made from intermediate Al standard solution (100 mg/L) prepared from Al stock solution (1000 mg/L) as follows: Al wire (1.000 g) was dissolved in a minimum amount of (1+1) HCl, a small drop of mercury was added as a catalyst. The solution was filtered to remove mercury and then diluted to 1000 mL with 1% (v/v) HCl. Aluminum standard stock solution (10 mL, 1000 mg/L) was pipetted into a 100-mL volumetric flask and diluted to the mark to make intermediate aluminum standard solution (100 mg/L). The aluminum standard concentrations (0, 2, 5, 10, 15, 20 and 25 mg/L) were prepared from intermediate aluminum standard solution (100 mg/L).

This was done by pipetting 0, 2, 5, 10, 15, 20 and 25 mL from the intermediate standard aluminum solution into 100-mL volumetric flasks and diluting to the mark. The standards were run on UV-visible spectrophotometer and a concentration versus absorbance calibration curve for the standards was generated. Then sample absorbances and concentration were read from the colorimeter (UV-Visible spectrophotometer).

3. Determination of anions: Sulfate, nitrate, chloride, fluoride, bicarbonate, phosphate and silica

Analysis of sulfate (SO₄²⁻): Sulfate (SO₄) in geothermal spring water samples was determined colorimetrically on UV-visible spectrophotometer (APHA, 1989). A calibration curve was generated from standard stock sulphate solution (100 mg/l) which was prepared by dissolving sodium sulphate (1.479 g) in distilled water and diluted to the mark in 1000-ml volumetric flask. Sulfate standard solution series for calibration were prepared from this stock solution by diluting 0, 2.0, 5.0, 10.0, 20.0 and 25.0 ml to 100 mL

to provide the following sulfate concentrations: 0, 2.0, 5.0, 10.0, 20.0, and 25.0 mg/L, respectively.

Then the standard sulfate solutions (100 mL) of concentrations 0, 2.0, 5.0, 10.0, 20.0, and 25.0 mg/L were transferred into 250-mL Erlenmeyer flask. A buffer solution (25.0 mL) was added and, while stirring, a spatulaful of barium chloride (BaCl₂) was added. After 60 seconds, absorbance was measured at 420 nm on UV-Visible Spectrophotometer. A calibration curve was prepared by relating absorbance of standards with their concentrations. Sulfate concentration in geothermal spring water samples was determined as follows: samples (100 mL) were each transferred into 250-ml Erlenmeyer flasks. A buffer solution (20.0 mL) was added into each sample and, while stirring, a spatulaful of BaCl₂ was added.

After 60 s, absorbance was measured at 420 nm on UV-Visible spectrophotometer. In order to make correction for sample colour and turbidity present in the original sample, blanks from which BaCl₂ was withheld were prepared and run. The sulfate concentrations in the samples were determined directly by referring to the calibration curve after subtracting blank absorbance from sample absorbance.

Determination of nitrate (NO₃⁻): A nitrate Ion-Selective Electrode (ELIT 8021), on a Mettler Toledo Seven Multimetre, was used to determine nitrate concentration in the geothermal spring water samples (APHA, 1989). Prior to sample reading, the electrode and meter were calibrated using sodium nitrate (NaNO₃) standard concentrations (1.0, 2.0, 5.0, 7.0 and 10.0 mg/L) prepared from the intermediate NaNO₃ standard (100 mg/L). This intermediate standard was prepared from 1000mg/L stock solution, which was again prepared by dissolving NaNO₃ (1.371g) which was dried at 105°C for 4 h. The standard concentrations were prepared by pipetting the following volumes from the intermediate NaNO₃ standard solution (100 mg/L) respectively: 1.0, 2.0, 5.0, 7.0, and 10 mL. These volumes were diluted to the mark in 100-ml volumetric flasks. Then the standards and samples (50 mL each) were carefully pipetted into 250-ml beakers separately. Ammonium sulfate ((NH₄)₂SO₄) (1.0 mL, 2.0 M) was added to these standards and samples as ionic strength adjustment buffer (ISAB) in order to ensure stable conditions before reading on the meter. Then after 20 min, NaNO₃ standards (1.0, 2.0, 5.0, 7.0 and 10.0 mg/L) were read from the meter as a means of electrode/ meter calibration. The nitrate concentrations of the samples were read from the meter.

Determination of chloride (Cl⁻): A chloride Ion-Selective Electrode (ELIT 8261) on a Mettler Toledo Seven Multi meter was used to determine chloride concentrations in the geothermal spring water samples (APHA, 1989). Before sample reading, the electrode and meter were calibrated using NaCl standard concentrations (1.0, 2.0, 5.0, 7.0, 10.0, 15.0 and 20.0 mg/L) prepared from the intermediate NaCl standard (100mg/L). The intermediate standard was prepared from 1000mg/L stock solution, which was again prepared by dissolving NaCl (1.649 g) dried at 110°C for 4 h. The standard concentrations were prepared by pipetting the following volumes from the intermediate NaCl standard solution (100 mg/L) respectively: 0, 2.0, 5.0, 7.0, 10.0, 15.0 and 20.0 ml. These volumes were diluted to the mark in 100-ml volumetric flasks. Then the standards and samples (50 ml each) were carefully pipetted into 250-ml beakers separately. Sodium nitrate (1 ml, 2% v/v, 5M) was added to 50ml of individual samples and standards, as Ionic Strength Adjustment Buffer (ISAB), to stabilize conditions before taking readings. Then after 20 min, NaCl standards (0, 2.0, 5.0, 7.0, 10.0, 15.0 and 20.0 mg/L) were read from the meter as a means of electrode/ meter calibration. Thereafter, the nitrate concentrations in the samples were read from the meter.

Determination of fluoride (F⁻): The fluoride ion-selective electrode Thermo Orion Ion Plus (9609BN) on a Mettler Toledo Seven Multimetre was used to determine fluoride concentration in the

geothermal spring water samples against the sodium fluoride (NaF) standard curve (APHA, 1989). The NaF standards (0, 2.0, 5.0, 10.0, 20.0 and 25 mg/L), prepared from intermediate NaF standard (100 mg/L), were used to calibrate the electrode and meter. This intermediate standard was prepared from NaF stock solution (1000 mg/L), which was again prepared by dissolving NaF (2.210 g) dried at 105°C for 6 h. The standard NaF concentrations were prepared by pipetting the following volumes from the intermediate NaF standard solution (100 mg/L) respectively: 0, 2.0, 5.0, 7.0, 10.0, 15.0 and 20.0 ml.

These volumes were diluted to the mark in 100-ml volumetric flasks. Total Ionic Strength Adjustment Buffer (TISAB) (25 mL) was added to 25 mL of individual samples and standards to adjust pH and reduce complex interferences before fluoride concentration reading in both standards and samples on the meter. Then after 20 min, NaF standards (0, 2.0, 5.0, 7.0, 10.0, 15.0 and 20.0 mg/L) were read from the meter as a means of electrode/ meter calibration. The nitrate concentrations of the samples were obtained directly from the meter.

Determination of bicarbonate (HCO₃⁻): Bicarbonates were determined using titrimetric method with hydrochloric acid (APHA, 1989). Hydrochloric acid (HCl) (0.02 M) was prepared by pipetting concentrated HCl (8.3 mL, 1.18 S.G) into 1000-mL volumetric flask and diluted to the mark with distilled water. Exactly 200mL of this stock solution was diluted to 1000 mL with distilled water which was standardized against sodium carbonate (Na₂CO₃, 0.0100 M). Na₂CO₃ (0.0100 M) was prepared as follows: anhydrous sodium carbonate (1.0599 g) previously dried at 250°C for one hour was dissolved in 300ml of distilled water, diluted to 1000-mL mark and stored in a polyethylene bottle. Then the prepared Na₂CO₃ solution (25.0 mL, 0.0100 M) was transferred into a 250-mL beaker, distilled water (25 mL) was added, and titrated with hydrochloric acid (0.02 M) to phenolphthalein end point. The resultant solution was boiled gently for 3-5 min, cooled to room temperature and titrated to bromocresol green/methyl red end-point.

The volume of the hydrochloric acid titrant used was (S), and concentration, M, of the hydrochloric acid was calculated as follows:

$$\text{Molarity (M)} = \frac{0.01 \times 25.0 \times 2}{S}$$

Samples were titrated in triplicates as follows: a sample of volume, V, (25 mL) was transferred into a 250-ml conical flask, phenolphthalein indicator solution (4 drops) were added and titrated with standard hydrochloric acid of concentration, M, until pink colour was just discharged.

The volume of titrant used was recorded as (P). Bromocresol green/ methyl red indicator (four drops) was added and titration was continued to a light pink colour. Total volume of titrant used was recorded as (T).

The bicarbonate concentration was calculated as follows:

$$\text{HCO}_3^- \text{ mg/L} = \frac{(T-2P) \times M \times 61000}{V}$$

Determination of phosphate (PO₄³⁻): The phosphate (PO₄³⁻) standards were used to generate a calibration curve in the UV-Visible Spectrophotometer from which the PO₄³⁻ concentrations in geothermal spring water samples were read (APHA, 1989).

The standard PO₄³⁻ solution (50 µg/mL) was prepared as follows: 3 g of potassium dihydrogen orthophosphate (KH₂PO₄) was dried on a watch glass at 105-110°C for overnight and cooled in a dessicator. KH₂PO₄ (0.9594 g) was weighed out and dissolved into a 500-ml volumetric flask with distilled water. This was 1 mg/ml PO₄³⁻

solution (standard stock solution).

For analysis, 5 ml of 1 mg/mL PO₄³⁻ solution was diluted to 100 ml with distilled water. This was 50 µg/mL PO₄³⁻ solution (intermediate standard solution). The PO₄³⁻ standard concentrations (0, 0.05, 0.1, 0.2, 0.3, 0.4 mg/L) were prepared from this intermediate standard solution by pipetting the following volumes into 100-mL volumetric flasks respectively and diluting them to the mark: 0, 1, 2, 4, 6 and 8 mL. Then the geothermal spring water samples (1 mL) were each pipetted into 100-mL beakers and into each beaker, HNO₃ (2 mL) and 5 mL of perchloric acid (HClO₄) were added. The resultant solution was heated on a hot plate until 2mL of solution remained (about 30 min) and then allowed to cool. HNO₃ (2 mL) and HClO₄ (5 mL) were added and the solution was again heated on the hot plate until 1 mL of solution remained. The solution was then allowed to cool.

Distilled water (20 mL) was added and the solution was heated gently (for 10 min, but it was not allowed to boil). The solution was decanted into a 100-ml volumetric flask and distilled water (70 mL) and reducing solution (20 mL) were added and the solution was diluted to volume with distilled water. This was left overnight before reading. The absorbance of the blank, standards and samples was measured at 555 nm.

Determination of silica (SiO₂): The first step was preparation of silica (Si) standards for derivation of a calibration curve from which Si concentration in the geothermal spring water samples were to be read on the UV-Visible spectrophotometer (APHA, 1989). From standard stock Si solution (1000 mg/L) (purchased), 5ml were pipetted into 500-mL volumetric flask and diluted to volume with distilled water.

Si standard volumes of 0, 2, 5, 10, 15 and 20 mL were measured from standard Si stock solution (0.01 mg/mL) using a 50-ml burette into 100-ml volumetric flasks. These standards contained the following concentration respectively: 0, 0.02, 0.05, 0.10, 0.15, and 0.20 mg/mL. Samples (1 mL) each were pipetted into clean nickel crucibles. Sodium hydroxide (2 g) was added and dissolved. The solution was heated over an open flame, starting with a small flame and gradually increasing the flame until the bottom of crucible was just red. Heating was continued for 3 min. Then the contents were removed and cooled. The crucible was then put into a 500-mL crucible polypropylene beaker. Hot distilled water was added into the crucible to dissolve the melt. The crucible was then removed, rinsed with hot distilled water and allowed to cool. The solution was then transferred into a 250-ml volumetric flask and diluted to the mark with distilled water. The solution was filtered through filter paper into a 500-ml propylene beaker. (First 10-20 mL solution was discarded).

The filtered solution was transferred to a plastic bottle to serve as sample stock solution. To sample stock solutions (1 ml) pipetted into 100-mL volumetric flasks in triplicates, P-nitrophenol indicator (1 drop) was added and acidified with drops of HCl (1+4) until the colour changed from yellow to colourless. The solution was diluted to about 50mL. To the mixture, HCl (1+4) (1 mL) and 5% ammonium molybdate solution (4 mL) were added and mixed thoroughly, allowed to stand for 10 min and 10% v/v tartaric acid solution (5 mL) and ascorbic acid solution (2 mL) were added. The resultant solution was diluted to the mark with distilled water, allowed to stand for 30 min at room temperature and absorbance and concentration of Si measured at 650nm wavelength. The SiO₂ were calculated from Si results.

Subsurface temperatures

The subsurface temperatures of geothermal springs in Nkhata Bay were determined using the following cation geothermometers: 1) Na/K chemical geothermometers by Truesdell (1976), Fournier

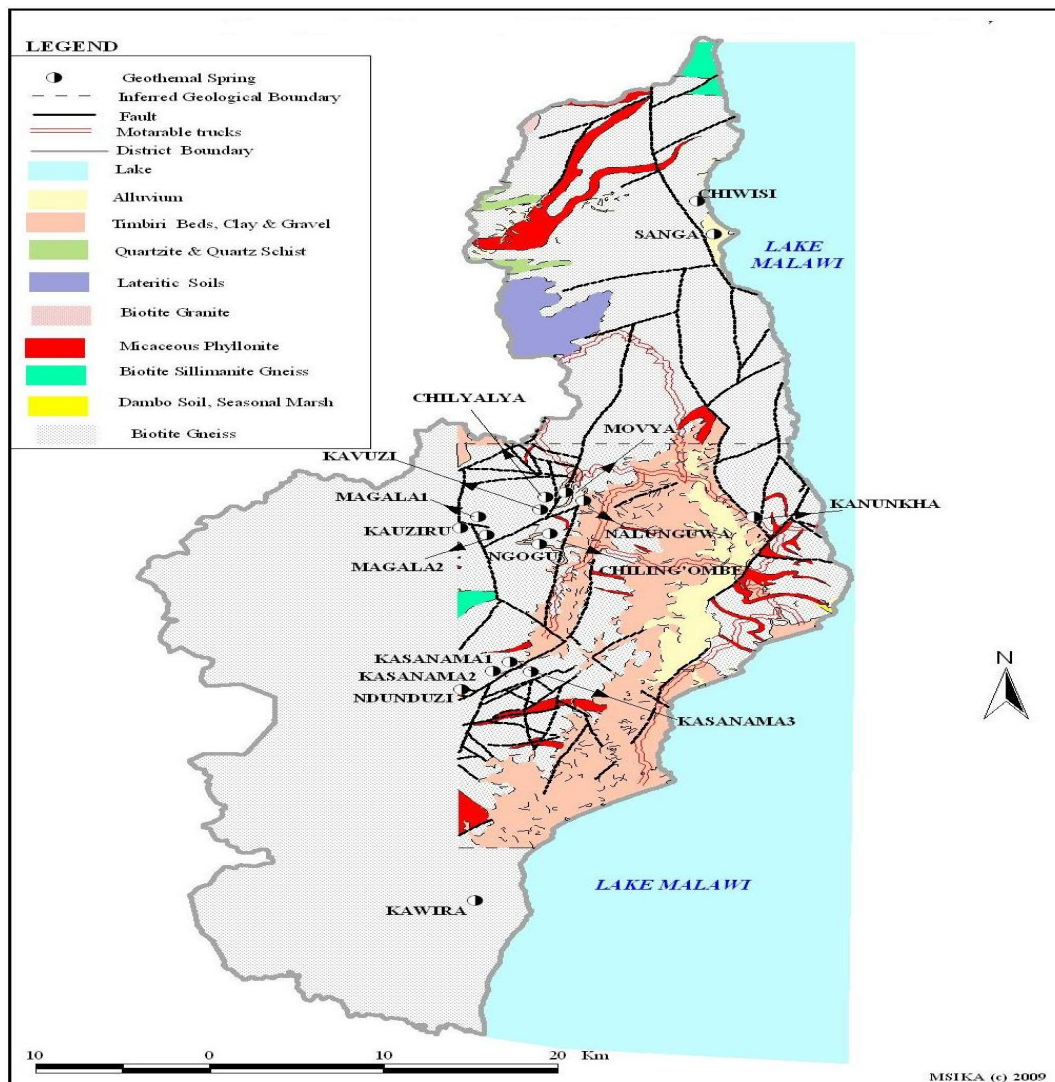


Figure 2. Spatial distribution of geothermal springs in Nkhata Bay, Malawi.

(1979), Arnorson (1983), Giggenbach (1988), and Verma and Santoyo (1997). These geothermometers have been coded as Na/K1, Na/K2, Na/K3, Na/K4 and Na/K5 respectively; 2) Na/K/Ca chemical geothermometer by Fournier and Truesdell (1973); and, 3) K/Mg chemical geothermometer by Giggenbach (1988).

RESULTS AND DISCUSSION

Spatial locations of geothermal springs in Nkhata Bay, Malawi

Seventeen geothermal springs, with surface temperatures ranging from 29±0.3 to 74±0.5°C, were identified and their distribution mapped in Nkhata Bay (Figure 2).

Spatially, 76% of the springs are clustered towards Nkhata Bay West and 94% of the springs characteristically occur along the major faults in the Basement

Complex in the District. Ostensibly, the spatial distribution of geothermal springs in the district is controlled by faulting which possibly provides conduits for hydrothermal convection in the Basement Complex (Figure 2).

Chemistry of geothermal springs

A summary of the chemistry of the thermal springs is provided in Table 1.

Physico-chemical characteristics of the geothermal springs

The surface temperature values of the thermal springs in Nkhata Bay ranged from 74.0±0.5 to 29.0 ±0.3°C. The

Table 1. Some chemical and physico-chemical characteristics of geothermal springs in Nkhata Bay, Malawi.

| Parameter (chemical species in mg/l) | Kawira | Kanunkha | Nalunguwa | Chilyalya | Kavuzi | Movya | Chiling'ombe | Ngogu | Magala1 | Kasanama1 | Kasanama3 |
|--------------------------------------|-------------|-------------|-------------------|-------------|------------|-------------|--------------|-------------|------------|------------|-------------|
| Na | 97.46±2.98 | 97.23±4.96 | 97.26±1.36 | 88.06±1.87 | 87.65±5.56 | 81.57±3.60 | 96.00±1.79 | 96.62±7.21 | 93.53± | 96.90±1.70 | 107.50±3.00 |
| K | 3.18±0.037 | 17.25±0.371 | 1.76±0.038 | 1.47±0.011 | 1.63±0.015 | 1.54±0.027 | 1.34±0.003 | 1.59±0.008 | 1.73±0.064 | 2.51±0.057 | 4.64±0.016 |
| Ca | 0.65±0.004 | 11.09±0.03 | 1.14±0.007 | 1.97±0.035 | 1.63±0.024 | 1.98±0.025 | 0.87±0.012 | 0.86±0.009 | 1.05±0.003 | 0.94±0.054 | 1.89±0.012 |
| Mg | 0.33±0.006 | 9.26±0.049 | 0.002±0.0002 | 0.24±0.001 | 0.17±0.002 | 0.07±0.002 | 0.06±0.001 | 0.15±0.001 | 0.08±0.002 | 0.02±0.003 | 1.32±0.014 |
| Fe | 0.66±0.044 | 27.23±0.103 | Not detected (Nd) | Nd | Nd | Nd | Nd | Nd | Nd | Nd | 1.40±0.133 |
| Cd | 0.033±0.007 | 0.049±0.007 | 0.020±0.008 | 0.023±0.010 | Nd | 0.001±0.009 | Nd | Nd | Nd | Nd | Nd |
| SiO ₂ | 0.16±0.007 | 0.44±0.020 | Nd | Nd | Nd | Nd | 0.02±0.007 | 0.05±0.007 | 0.08±0.007 | 0.17±0.003 | 0.20±0.011 |
| F ⁻ | 10.27±0.25 | 7.31±0.10 | 3.29±0.07 | 2.78±0.19 | 2.73±0.03 | 2.55±0.24 | 2.47±0.03 | 3.16±0.17 | 2.21±0.06 | 5.67±0.01 | 5.39±0.14 |
| Cl ⁻ | 6.49±0.83 | 14.73±0.56 | 9.55±0.20 | 7.62±0.10 | 8.74±0.27 | 7.26±0.13 | 5.64±0.87 | 5.57±0.12 | 11.68±0.36 | 6.17±0.10 | 5.61±0.17 |
| HCO ₃ ⁻ | 67.21±9.60 | 96.02±13.58 | 43.21±4.8 | 76.81±0.00 | 43.01±6.80 | 76.81±0.00 | 52.81±4.80 | 76.81±0.00 | 48.01±0.00 | 52.81±4.80 | 33.61±4.81 |
| SO ₄ ²⁻ | 46.02±2.73 | 106.52±2.10 | 99.82±0.86 | 85.86±4.83 | 93.52±2.35 | 87.48±2.85 | 60.55±2.10 | 123.63±3.98 | 55.92±0.63 | 86.98±0.99 | 53.16±3.14 |
| Ionic Strength | 0.0041 | 0.0070 | 0.0046 | 0.0045 | 0.0045 | 0.0040 | 0.0055 | 0.0039 | 0.0049 | 0.0047 | 0.0041 |
| Temp (° C) | 74.0±0.5 | 53.2±0.5 | 39.5±1.8 | 46±0.0 | 50.3±1.0 | 41.2±0.3 | 40.4±0.3 | 39.0±1.0 | 48.3±0.6 | 61.5±1.3 | 65.0±0.0 |
| pH | 8.12±0.09 | 6.50±15 | 8.65±0.12 | 8.23±0.12 | 7.64±0.04 | 8.08±0.05 | 8.27±0.10 | 8.43±0.11 | 7.89±0.23 | 8.36±0.07 | 8.39±0.14 |
| EC (µS/cm) | 5267±153 | 7183±76 | 5300±0.0 | 4767±58 | 5183±104 | 4430±20 | 4917±176 | 4617±29 | 4800±0.0 | 6393±51 | 6810±193 |

electrical conductivities ranged from 7183- 4430 µS/cm (Table 1). The pH in the geothermal springs studied was in the range of 6.5-8.65. Water with a pH below 6.5 is considered acidic and a pH above 8.5 is considered basic (GNWT, 2008). Thus, practically all the studied thermal spring waters are of neutral type. The exception is Nalunguwa, which is slightly alkaline (Table 1).

Chemical characteristics

Sodium (Na) represented the highest concentration values in almost all the studied geothermal springs, this was followed by sulfate (SO₄²⁻), bicarbonate (HCO₃⁻), chloride (Cl⁻), fluoride (F⁻), potassium (K), calcium (Ca), nitrate (NO₃⁻), magnesium (Mg) and Cadmium (Cd) - in descending order of

abundance. Thus, in terms of cations, Na is followed by K in abundance in the geothermal springs.

However, unlike Na (>80 mg/L), the concentration of K is considerably lower (<10 mg/L) in most thermal springs in Nkhata Bay. With regard to anions, the following is their descending order of abundance (mg/L): SO₄²⁻ > HCO₃⁻ > Cl⁻, > F⁻ > NO₃⁻.

Lead (Pb), chromium (Cr) and phosphate (PO₄³⁻) were below detection limits in all the studied geothermal springs. Trilinear Piper plot (Figure 3) was used to delineate the principal hydrochemical characteristics of the thermal springs.

The trilinear piper plot hydrochemically distinguished two water facies of geothermal springs: 1) sodium - sulfate (Na-SO₄) water type for

Kasanama1 and Nalunguwa geothermal springs and 2) Sodium- sulfate-bicarbonate (Na-SO₄-HCO₃) water type for Kawira, Kanunkha, Movya, Chilyalya, Chiling'ombe, Ngogu, Magala1 and Kasanama3 springs.

Equilibrium conditions and water quality of geothermal springs in Nkhata Bay, Malawi

Several mineral species in contact with the thermal waters and equilibrium conditions (as reflected by the saturation indices (SI)) in the geothermal springs in Nkhata Bay were monitored and analyzed using AquaChem 5.1 software (SWS, 2008).

The following mineral species were inferred to have been in contact with the geothermal

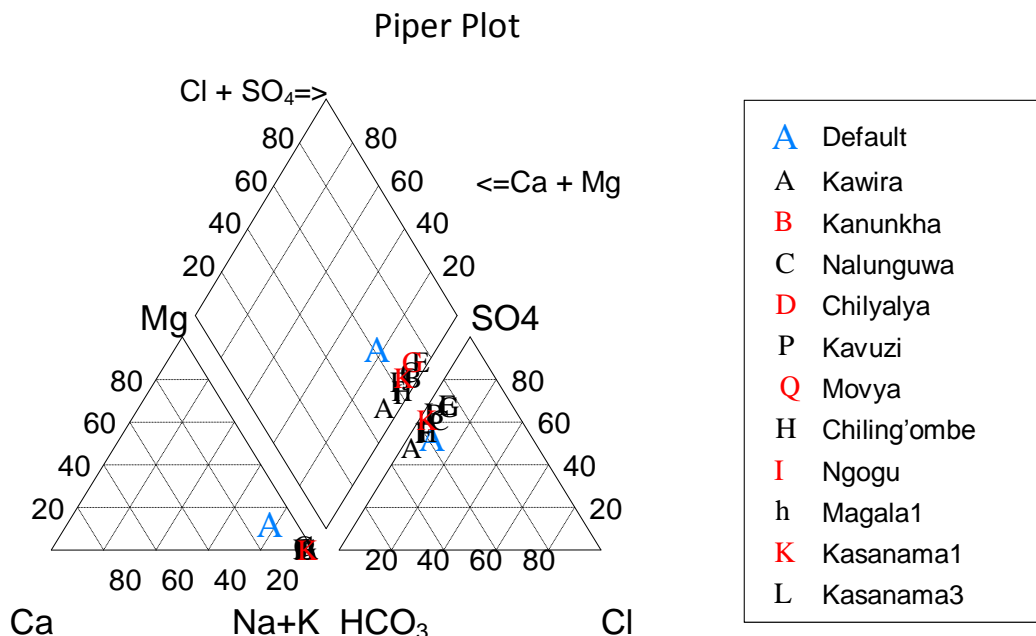


Figure 3. Principal chemistry of the water facies of geothermal springs in Nkhata Bay.

spring waters in the district: calcite, aragonite, dolomite, gypsum, anhydrite, halite, fluorite, goethite, siderite and haematite.

There was undersaturation ($SI < 0$) in all of the springs with respect to the following mineral species: calcite (CaCO_3), aragonite (CaCO_3 in its rhombic form, harder and less common or stable than calcite), dolomite ($\text{CaMg}(\text{CO}_3)_2$), anhydrite (CaSO_4), halite or rock salt (NaCl), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and fluorite or fluorospar (CaF_2). However, there was supersaturation ($SI > 0$) with respect to goethite ($\text{FeO}(\text{OH})$), haematite (Fe_2O_3) and siderite (FeCO_3) in Kanunkha, Kawira, Nalunguwa and Kasanama3 thermal waters.

Water, which is calcite-undersaturated ($SI(\text{calcite}) < 0$), is corrosive to the pipes and on the other hand, if the water is calcite-oversaturated ($SI(\text{calcite}) > 0$), the calcite precipitates out and settles on the pipelines (Purschel, 2006).

Similarly, siderite, goethite and haematite ($SI > 0$) precipitate and settle down in the springs in which they are inferred, unlike calcite, aragonite, halite, gypsum, anhydrite and fluorite ($SI < 0$) which suggestively remain in thermal water column.

Despite fluorite undersaturation in the studied geothermal springs, fluoride concentration (Table 1) was high in all of them (> 1.5 mg/L, WHO guidelines for drinking water). Moreover, due to the undersaturation conditions, fluoride cannot precipitate as CaF_2 , and so mobilizes freely without forming other complexes in the thermal waters as also observed by Rango et al. (2008). Chronic ingestion of concentrations much greater than 1.5 mg/L is linked with development of dental fluorosis and, in

extreme cases, skeletal fluorosis; high doses have also been linked to cancer (BGS, 2008).

Iron (Fe) levels observed in Kawira, Kanunkha and Kasanama3 thermal springs exceeded the safe limit of 0.20 mg/L set by MBS. High levels of iron oxides may result in development of a benign pneumoconiosis, called siderosis (lenntech, 2006).

The cadmium (Cd) levels observed in Kawira, Kanunkha, Nalunguwa and Chilyalya geothermal springs exceed the safe limit of 0.005 mg/L set by both MBS and WHO. Except Chilyalya which occurs on a hill where no farming takes place, the cadmium levels in other springs are likely to be exacerbated by phosphate fertilizer, which is commonly used in the farming field along the banks since fertilizer is a natural sink of cadmium.

Recent data indicate that adverse health effects of cadmium exposure may occur at lower exposure levels than previously anticipated, primarily in the form of kidney damage but possibly also bone effects and fractures (Järup, 2003).

The EC range of 7183- 4430 $\mu\text{S}/\text{cm}$ in thermal waters in Nkhata Bay exceeds the WHO recommended EC value in surface water of 2500 $\mu\text{S}/\text{cm}$.

The pH of most of these thermal waters was within 6.5-8.5 (recommended limit, WHO water quality criteria) except Nalunguwa thermal waters which were slightly alkaline (pH = 8.65).

The extent of equilibrium conditions in the studied geothermal springs in Nkhata Bay is been represented in Figure 4. The Gibbenbach Triangle, the triangular K-Mg-Na representation by Giggenbach(1988), allows the verification of the extent to which water-rock

Giggenbach Triangle

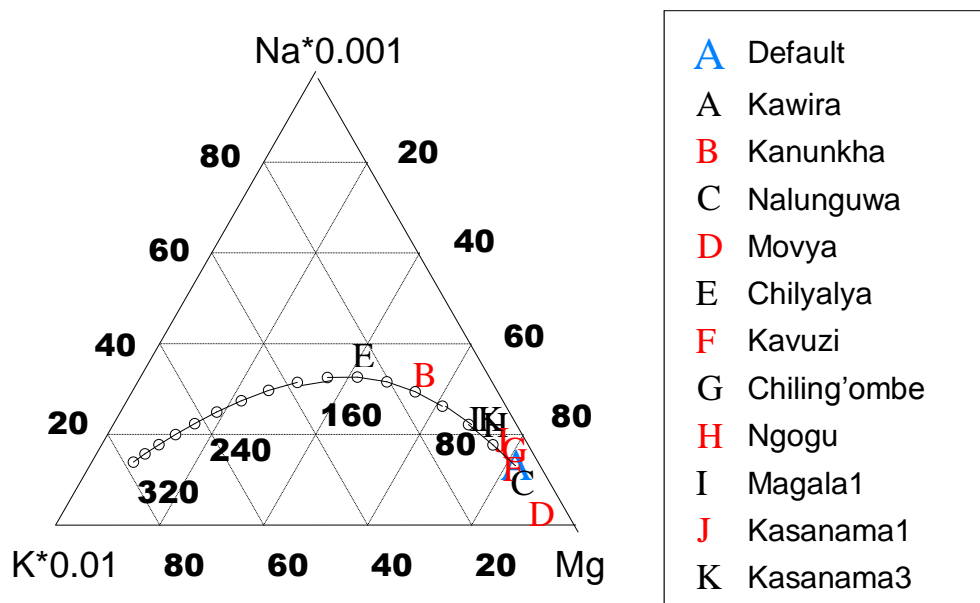


Figure 4. Extent of water-rock equilibrium in geothermal springs understudy.

equilibria have been attained in the reservoirs (SWS, 2008). The triangle (Figure 4) comprises three zones: Immature waters (at the base); Partially equilibrated waters (in the middle); and Fully equilibrated waters (along the curve).

Except Movya which reflects immature water, Kavuzi, Chilyalya, Nalunguwa, Chiling'ombe, Ngogu, Magala1, Kawira, Kanunkha, Kasanama1 and Kasanama3 geothermal springs reflect fully equilibrated waters (Figure 4).

Since the Giggenbach Triangle (Giggenbach, 1988) indicates that most of the geothermal springs studied in Nkhata Bay have fully equilibrated waters, their chemistry can reliably be used to calculate the probable subsurface temperatures at which water-rock equilibria were attained.

Subsurface temperatures of geothermal springs in Nkhata Bay

Three cation geothermometers (Na/K, Na/K/Ca and K/Mg) geothermometers were considered for estimating the sub-surface temperature of the geothermal springs in Nkhata Bay.

Na/K geothermometer usually offers the best chemical indication of high temperatures at depth since the Na/K ratio is low in hot areas and high in cool areas (Elder, 1981). These chemical constituents of the hot water are leached from geological sources in such a manner that at higher temperatures, there is an increased tendency for

K to replace Na in feldspars (Elder, 1981).

The chemical reaction that occurs is reflected in the chemical Equation (1).



Further, Na/K geothermometers are not affected by any concentration-dilution process since alkali metals are generally aquaphilic and their ratio is not affected by the kinetics of the reservoir (CER, 2007). They can, thus, be indicative of the highest temperature at which the waters have reached at chemical equilibrium with the reservoir rocks.

Evident from Table 2, only cation (Na/K, Na/K/Ca and K/Mg) geothermometers were considered for sub-surface temperature estimation of the geothermal springs in Nkhata Bay. Silica geothermometers were not considered relevant in this study because they gave subsurface temperature values which were too inconsistent to be plausible (Appendix 2).

The values were, thus, too low for most silica geothermometers and too high for one geothermometer. For example; silica (SiO_2) geothermometer models by Truesdell (1976), Fournier (1977) and Verma and Santoyo (1997) gave values which were too low ($<0^\circ\text{C}$) while one model by Rimstidt (1979) gave temperatures values which were too high ($> 500 \leq 40922^\circ\text{C}$) - the reason being that silica was found in very low concentrations in geothermal springs understudy (Table 1). This was probably because of dilution that might have

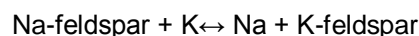
Table 2. Sub-surface temperatures of Nkhata Bay geothermal springs estimated using some cation (Na/K, Na/K/Ca and K/Mg) geothermometers.

| Geothermal Spring | Measured temperature (°C) | Na/K ₁ (°C) | Na/K ₂ (°C) | Na/K ₃ (°C) | Na/K ₄ (°C) | Na/K ₅ (°C) | Na/K/Ca ₁ * (°C) | K/Mg (°C) |
|-------------------|---------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|-----------------------------|-----------|
| Kawira | 74 | 92 | 137 | 103 | 156 | 142 | 144 | 26 |
| Kanunkha | 53 | 259 | 272 | 262 | 283 | 272 | 209 | 26 |
| Nalunguwa | 39.5 | 56 | 104 | 68 | 125 | 111 | 114 | 10 |
| Movya | 41 | 52 | 100 | 64 | 121 | 107 | 85 | 31 |
| Chilyalya | 46 | 58 | 106 | 69 | 126 | 112 | 93 | 29 |
| Kavuzi | 50 | 59 | 106 | 70 | 127 | 113 | 86 | 26 |
| Chiling'ombe | 40 | 42 | 91 | 54 | 112 | 98 | 106 | 26 |
| Ngogu | 39 | 51 | 99 | 63 | 120 | 106 | 113 | 29 |
| Magala1 | 48 | 57 | 105 | 69 | 126 | 112 | 116 | 25 |
| Kasanama1 | 61.5 | 77 | 123 | 89 | 143 | 129 | 131 | 16 |
| Kasanama3 | 65 | 112 | 154 | 123 | 173 | 159 | 150 | 29 |

*No Mg-correction was done on geotemperature values for Na/K/Ca geothermometer.

occurred as a result of mixing between thermal and ambient ground waters. On the other hand, this could also be due to silica precipitation that might have happened prior to the collection of geothermal water samples for analysis as was also observed in one study conducted by Wahl (1977).

In this study, however, most Na/K geothermometers were used to estimate geotemperatures of the thermal springs, considering that the best chemical indications of high temperatures at depth are given by the Na/K ratio which, for example, is low in hot areas and high in cool areas (Elder, 1981). These chemical constituents of the hot water are leached from geological sources in such a manner that at higher temperatures, there is an increased tendency for K to replace Na in feldspars (Elder, *ibid*). The chemical reaction that occurs is reflected in the chemical equation:



CER (2007) also observes that Na/K geothermometers are not affected by any concentration-dilution process since alkali metals are generally aquaphilic and their ratio is not affected by the kinetics of the reservoir. Therefore, they can be indicative of the highest temperature at which the waters have reached at chemical equilibrium with the reservoir rocks (CER, 2007).

The deep reservoir temperatures in the geothermal springs in Nkhata Bay ranged from 112 to 283°C, estimated using Na/K geothermometers (Table 2). Similarly, Na/K/Ca geothermometer gave a subsurface temperature range of 85 - 209°C in the thermal springs. On the contrary, the K/Mg geothermometer gave a subsurface temperature range of 10 to 29°C for geothermal springs in Nkhata Bay. The highest geotemperatures were associated with Kanunkha, Kawira and Kasanama3 geothermal springs; the lowest geotemperatures were

associated with Chiling'ombe and Ngogu geothermal springs.

Pirlo (2004) indicated that the better the correlation between the emergence spring temperatures and subsurface temperatures estimated by the geothermometer, the better the geothermometer becomes for efficient use in a particular hydrothermal system.

From the correlation analysis conducted using Genstat 12.0 Software (NAG, 2008), Na/K/Ca geotemperatures showed the strongest positive correlation with measured temperatures of the geothermal springs ($r = 0.50$) and a geotemperature range of 85 - 209°C has been estimated for geothermal springs in Nkhata Bay.

Similarly, Na/K geotemperatures showed relatively strong positive correlation with the measured (emergence) temperatures of the geothermal springs ($r \geq 0.36$, $P < 0.01$).

In particular, Na/K₄ geotemperatures displayed the strongest positive correlation with the measured temperatures of the thermal springs ($r \geq 0.39$, $P < 0.01$). Using Na/K₄ geothermometer, the geotemperature range of 112 - 283°C was estimated for geothermal springs in Nkhata Bay. On the contrary, K/Mg geothermometer that gave the lowest geotemperatures (Table 2), had the weakest positive correlation with the measured temperatures of the geothermal springs ($r \geq 0.03$, $P < 0.01$).

Hong et al. (2005) observe that K/Mg geothermometers can only be used for chloride waters as it is sensitive to mixing. The low geotemperatures given by K/Mg geothermometers can be attributed to very low Mg content (<1 mg/L) in most thermal waters under study (Table 1) possibly due to dilution as a result of mixing between thermal waters and ambient groundwater.

To this end, it seems, therefore, that the Na/K/Ca and Na/K geothermometers offer better and more robust

estimates of original subsurface temperatures of geothermal springs in Nkhata Bay; they both gave significant positive correlation with the emergence temperatures of the springs ($p < 0.01$).

Conclusion

The chemistry of geothermal springs in Nkhata Bay reveals two spring water types: (1) sodium-sulfate (Na-SO₄) springs, which include Nalunguwa and Kasanama1 geothermal springs; and, (2) sodium-sulphate-bicarbonate (Na-SO₄-HCO₃) springs, which include Kawira, Kanunkha, Movya, Chilyalya, Ngogu, Chiling'ombe, Magala1 and Kasanama3 geothermal springs. Except Movya which has immature water, all these thermal springs have fully equilibrated waters.

The chemistry of geothermal springs in Nkhata Bay, Malawi, evidently shows that utilization of the thermal waters for drinking is not suitable due to high fluoride concentrations (> 1.5 mg/L, WHO guidelines for drinking water) and high EC values (> 2500 μScm^{-1} , WHO recommended EC value).

In addition, high concentrations of iron (Fe) (> 0.20 mg/L set by MBS) and cadmium (> 0.005 mg/L, safe limit set by both MBS and WHO) were determined in several thermal springs in the District, such as Kawira, Kanunkha, Kasanama3, Nalunguwa and Chilyalya. The original subsurface temperatures of Nkhata Bay geothermal springs, estimated by the Na/K/Ca and Na/K geothermometers, ranged from 85 to 209 and 112 to 283°C, respectively. The highest geotemperatures were associated with Kanunkha, Kawira and Kasanama3 geothermal springs; the lowest geotemperatures were associated with Chiling'ombe and Ngogu thermal springs.

The Na/K/Ca and Na/K geothermometers were found to provide better and more robust estimates for subsurface temperatures (geotemperatures) of geothermal springs in Nkhata Bay as these most significantly ($p < 0.01$) correlated with the emergence temperatures of the thermal springs with correlation coefficient (r) = 0.50 and $r \geq 0.36$ for Na/K/Ca and Na/K geotemperatures, respectively. The estimation of subsurface temperature in the geothermal springs in Nkhata Bay, however, needs re-evaluation by use of more extensive hydrogeochemical and geophysical surveys in order to establish whether they can be used for generation of geothermal electricity in Malawi.

Conflict of Interests

The author(s) have not declared any conflict of interests.

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Appendix 1. Spatial data for geothermal springs in Nkhata Bay, Malawi.

| Geothermal spring | utm coordinates | Village | Traditional authority |
|-------------------|------------------|------------------|-----------------------|
| Kawira | 0610504; 8665862 | Chaphulika | Zilakoma |
| Kanunkha | 0635870; 8718574 | Chighachang'ombe | Timbiri |
| Nalunguwa | 0620479; 8720782 | Chilongozi | Kabunduli |
| Movya | 0618818; 8721976 | Chilongozi | Kabunduli |
| Chilyalya | 0618291; 8721782 | Chamawoya | Kabunduli |
| Kavuzi | 0618187; 8721622 | Chamawoya | Kabunduli |
| Chiling'ombe | 0616070; 8715216 | Kachiweya | Kabunduli |
| Ngogu | 0616096; 8714990 | Kachiweya | Kabunduli |
| Kasanama1 | 0614246; 8697772 | Chilipeta II | Kabunduli |
| Kasanama2 | 0614163; 8697752 | Chilipeta II | Kabunduli |
| Kasanama3 | 0615297; 8698416 | Chilipeta II | Kabunduli |
| Ndunduzi | 0609352; 8694896 | Chilipeta II | Kabunduli |
| Magala1 | 0610111; 8716546 | Vimaso | Kabunduli |
| Magala2 | 0610164; 8716592 | Vimaso | Kabunduli |
| Kauziru | 0609554; 8716788 | Vimaso | Kabunduli |
| Chiwisi | 0630933; 8761965 | Siyalimba | Musisya |
| Sanga | 0632384; 8757501 | Kajizinge | Musisya |

Appendix 2. Geotemperatures estimated by silica geothermometers for thermal springs in Nkhata Bay, Malawi.

| Spring name | Measured Temperature (°C) | QTZ ₁ | QTZ ₂ | QTZ ₃ | QTZ ₄ | QTZ ₅ |
|--------------|---------------------------|------------------|------------------|------------------|------------------|------------------|
| Kawira | 74 | -41.37 | -41.82 | 2089.63 | -81.19 | -73.09 |
| Kanunkha | 53 | -21.81 | -22.23 | 40921.95 | -46.02 | -54.36 |
| Nalunguwa | 39.5 | - | - | - | - | - |
| Movya | 41 | - | - | - | - | - |
| Chilyalya | 46 | - | - | - | - | - |
| Kavuzi | 50 | - | - | - | - | - |
| Chiling'ombe | 40 | -74.00 | -74.45 | 518.75 | -154.97 | -103.63 |
| Ngogu | 39 | -59.80 | -60.26 | 881.68 | -120.11 | -90.45 |
| Magala1 | 48 | -53.05 | -53.50 | 1165.38 | -105.11 | -84.12 |
| Kasanama1 | 61.5 | -40.35 | -40.80 | 2221.82 | -79.22 | -72.13 |
| Kasanama3 | 65 | -37.13 | -37.57 | 2747.08 | -73.08 | -69.06 |

QTZ₁: Silica geothermometer by Trusdell (1976)

$$\text{Formula: } T_{\text{SiO}_2} = \frac{1315 - 273.15}{5.205 - \log m}$$

QTZ₂: Silica geothermometer by Fournier (1977)

$$\text{Formula: } T_{\text{SiO}_2} = \frac{1309 - 273.15}{5.19 - \log m}$$

QTZ₃: Silica geothermometer by Rimstidt (1997)

$$\text{Formula: } T_{\text{SiO}_2} = (856 / \log m) + 0.0254 - 273.15$$

QTZ₄: Silica geothermometer by Verma and Santoyo (1997)

$$\text{Formula: } T_{\text{SiO}_2} = -44.119 + (0.24469m) + ((-1.7414 \times 10^{-4}) m^2) + (79.305 \times \log m)$$

QTZ₅: Silica geothermometer by Fournier (1977)

$$\text{Formula: } T_{\text{SiO}_2} = \frac{1032 - 273.15}{4.69 - \log m}$$

Note: m = concentration of SiO₂ in ppm or mg/L.