

UNIVERSITY OF NAIROBI
COLLEGE OF BIOLOGICAL AND PHYSICAL SCIENCES
SCHOOL OF PHYSICAL SCIENCES

**Effects of sea water intrusion on the chemistry of hotsprings:
A comparative study between Majimoto hotsprings in the Kenyan South
Coast and Bogoria Hotsprings in the Rift Valley**

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I56/60289/2011

**A dissertation submitted in partial fulfillment of the requirements for the degree of Master
of Science in Applied Geochemistry**

JULY, 2014

Declaration

This thesis is my original work and has not been presented for a degree in any other university or any other award.

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Abstract

The Majimoto hot springs are located outside the active volcanic Rift Valley in the Kenyan coast. They lie on south of the Kenyan Coast in the Kwale district. The hot springs are located approximately 18kms from the Indian Ocean and are important since they manifest geothermal potential in the area. Three hot springs occur in the vicinity with temperatures ranging from 55-70°C and an average flow rate of approximately 90 l/s. The project presents the evaluation of geochemical results of the sampled three hot springs in Majimoto, three hot springs from Bogoria and the sea water with the aim of evaluating sea water influence in the Majimoto hot springs. Majimoto hot springs give unreliable geothermometry temperature due to the influence of the sea water in its chemistry. Due to this, it is necessary to recalculate the chemistry of the hot spring to find out the actual chemistry of the hot spring without the sea water and find out the actual characteristics of the reservoir that hosts the hot spring. The study was done in Majimoto hot springs which are located outside the active volcanic Rift Valley in the Kenyan coast and the results compared with the chemistry of Bogoria hot springs located within the Rift floor which are free from sea water contamination. The Majimoto hot springs are located approximately 18kms off the Indian Ocean and are important since they manifest geothermal potential in the area. Three hot springs occur in the vicinity with surface temperatures ranging from 55-70°C and an average outflow rate of approximately 90 l/s. The project presents the evaluation of geochemical results of the sampled three hot springs in Majimoto, three hot springs from Bogoria and the sea water with the aim of evaluating sea water influence in the Majimoto hot springs. The Majimoto hot springs are characterized by NaCl-NaHCO₃ waters, suggesting that the springs are most likely being controlled underneath by an intrusive hot body. Bogoria hot springs are characterized by Na-HCO₃ type of waters. The major thermal manifestations within this Bogoria are geysers, hot springs and fumaroles which can be observed along the shores of the lake with surface temperatures ranging from 85-98°C. The results indicate that 3% of sea water is found in the Majimoto hot springs. The Na-K-Mg ternary denotes that the original Majimoto chemistry hot springs compares with sea water. Geothermometry temperature calculations display a 5°C temperature difference between the original and recalculated Majimoto hot spring water. The comparative K/Mg vs. K/Ca plot designates that the Majimoto hot springs waters are either mixed or part of a flow-through type convective system. Sea water is also typical of Na-Cl type of water. Further work involving a numerical model to investigate the occurrence of sea water

intrusion in Majimoto and hydrogeochemical processes that may accompany sea water intrusion into these hotsprings should be carried out in order to support and validate the presence of sea water in Majimoto hotsprings.

Acknowledgement

First and foremost I would like to express my sincere gratitude to Jehovah, THE ALMIGHTY GOD, for giving me this rare chance to undertake this course more so, for giving me the strength and will to undertake this project.

I would also like to express my sincere gratitude to the University of Nairobi for giving the opportunity and chance by awarding me with a scholarship to undertake this Masters of Geology course in Applied Geochemistry. I wish also to thank Prof. D. Olago my project supervisor for his continuous support and encouragement throughout the course.

I also wish to thank Dr. C. Nyamai, my second supervisor and also the chairman of the department, for his continuous support in my project and his timely responses during my project work.

I wish also to thank Dr. L. Olaka for her valuable encouragements, suggestions and comments towards the realization of this project.

I also wish to appreciate Mr. C. Wanjie for his valuable discussions and provision of data during my project work.

My sincere gratitude goes to Geothermal Development Company for allowing me to use data from Majimoto and Bogoria geothermal prospect. Most important I would like to thank my fellow course students for their friendship and warmth that existed.

Dedication

øTo JEHOVAH EL SHADDAIö

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List of abbreviations and symbols

NaCl-NaHCO ₃	Sodium chloride-sodium bicarbonate water type
Pb	Lead
Zn	Zinc
Cu	Copper
Fe	Iron
3-D	Three dimensional
H ₂ S	Hydrogen sulphide gas
CO ₂	Carbon dioxide gas
WNW	West-North-West direction
ENE	East- North-East direction
NNE	North-North East direction
SSW	South- South West direction
ESE	East-North East direction
WSW	West-South West direction
SO ₄	Sulphate anion
F ⁻	Fluoride anion
BaSO ₄	Barium sulphate
Cl-Li-B	Chloride-Lithium-Boron ternary diagram
Na-K-Mg	Sodium-Potassium- Magnesium ternary diagram
Cl-SO ₄ -HCO ₃	Chloride-Sulphate-Bicarbonate ternary diagram
TNa/K	Estimated Na/K geothermometer temperature
TK/Mg	Estimated K/Mg geothermometer temperature

Chapter 1

1. Introduction

The Majimoto and Bogoria hot springs are located in Kwale County in the south Coast of the Kenya and Baringo County in Central Rift Valley respectively (Eshimwata and Mwinami, 2011, Karingithi and Wambugu, 2008) (see Figure 1.1). The hot springs of Majimoto are located approximately 18 kilometers north of the Indian Ocean (Figure 2.2). Hot springs are important since they manifest the geothermal potential in an area. The chemistry of these hot springs is important in determining the geothermometry temperatures of the reservoirs that hosts the hot springs. Geothermometry temperatures are important in estimating reservoir temperatures in geothermal systems. Unreliable geothermometry temperatures may be due to sea water influence or interaction with surface cool meteoric waters. This study seeks to explore the effects of sea water on the chemistry of Majimoto hot springs in the Kenyan Coast by comparing the results with the Bogoria hot springs within the Rift Valley which are free from sea water contamination. Majority of the studies undertaken that touched on sea water intrusion have focused on sea water influence to coastal aquifers. Very few studies have been done that touch on the influence of the sea water on the chemistry of hot springs worldwide.

Sea water intrusion in coastal aquifers is usually a common contamination problem that occurs in the coastal areas (El-Bihery and Lachmar, 1994). Generally, coastal areas comprise lowlands with small gradients bordering estuaries/sea and the lower reaches of rivers, coastal marshes, lagoons and in rare cases hot springs. The economic significance of coastal regions requires no elaboration as many of the world's largest cities are near to the sea and about one third of the human habitats are within a 100 kilometers strip along the coastal line (Frind, 1982, Bond and Bredehoeft, 1987, Bear, 1999).

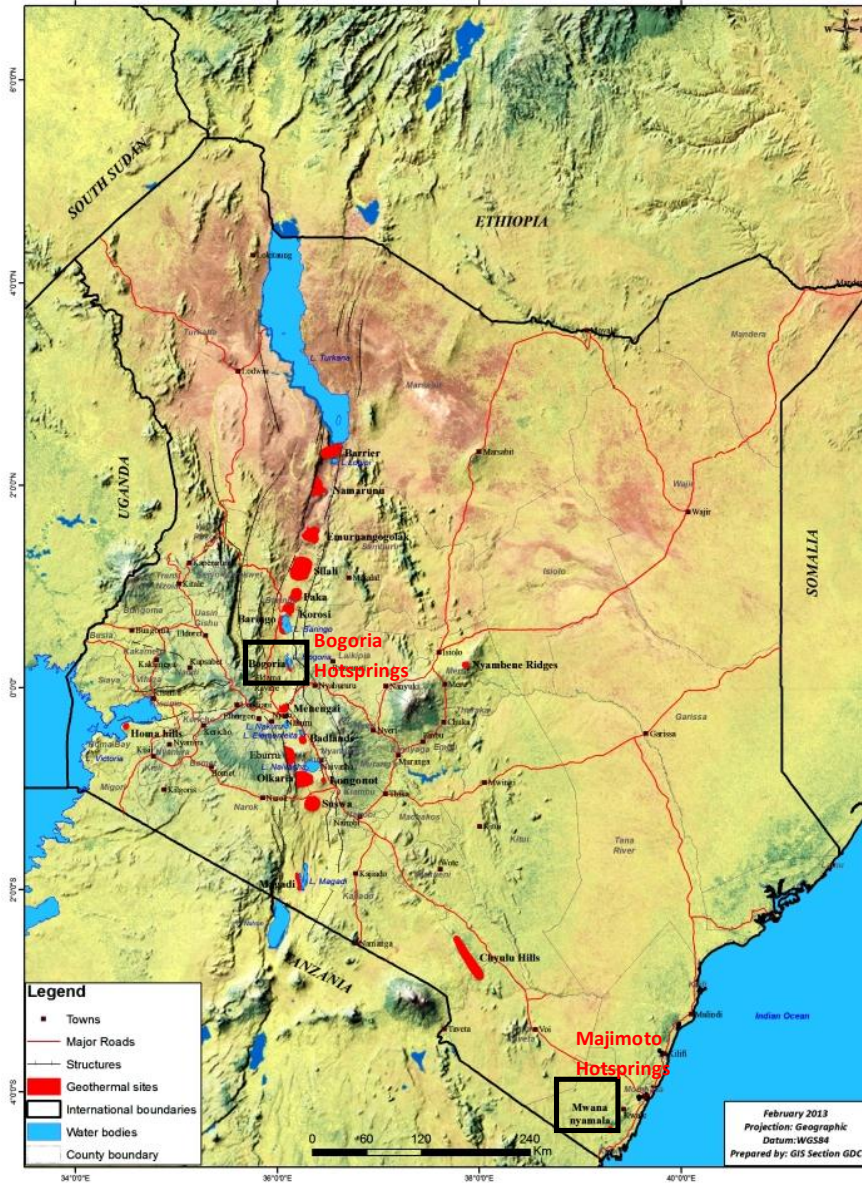


Figure 1.1: Map showing the location of the hot springs within the study area

Since coastal areas are characterized by the interaction of land, sea and the atmosphere there is a large possibility of interaction of the sea water with the hot springs water. Therefore, there is need to understand the effect of the sea water on the chemistry of the hot springs. In this study the chemistry of the Majimoto hot springs will be investigated to uncover the proportion of sea water in the hot springs water and also understand the effects of sea water intrusion into these hot springs. The results will then be compared with the chemistry of the Bogoria hot springs which are located in the Rift and are free from sea water interference. The Bogoria waters where

included in this study since they were used to find out if the Majimoto waters were affected by the sea water.

1.1. Process of Sea water Intrusion

The migration of sea water into fresh water aquifers under the influence of groundwater development is termed as sea water intrusion (Freeze and Cherry, 1979). There is usually a likelihood of intrusion of salt water both into surface water bodies including fresh water aquifers and hot springs in low lying coastal areas. Saline water originates mainly from the sea into open estuaries. Penetration of the sea water into rivers is induced by the density difference between fresh and saline water and also due to head differences during low-river-flow. Normally, the denser saline water forms a deep wedge that is separated from fresh water by a transition zone. Under unperturbed conditions, the saline water body remains stationary, its position being defined by the fresh water potential and hydraulic gradient (Kishi et al., 2000). But when the aquifer is disturbed by activities like pumping of freshwater or changing recharge conditions, the saline water body may gradually advance until a new equilibrium state is reached. The problem arises when saline water from the deeper saline wedge enters the wells thereby affecting the water quality (Bear, 1999). Hot springs under coastal areas may become saline due to overdraft of the recharge water pockets, reclamation of low-lying recharge areas, tidal effects, sea level changes, as well as aquaculture and fisheries activities in recharge areas (Freeze and Cherry, 1979).

Saltwater intrusion is driven by transport of saltwater due to advection and dispersion. The process by which solutes are transported by the bulk motion of the flowing groundwater is termed as advection. However, there is a tendency for the solute to spread out from the path and this spreading process is called hydrodynamic dispersion (Freeze and Cherry, 1979). Dispersion is due to the combined action of both a purely mechanical phenomenon and a physio-chemical phenomenon. The mechanical dispersion is produced by non-uniform velocity distribution of the fluid flow, due to boundary effects acting in the three different ways: (i) the velocity is zero on the solid surface, which creates a velocity gradient in the fluid phase; (ii) the variation of the pore spaces causes discrepancies between the maximum velocities along the pore axes; and (iii) the streamlines fluctuate with respect to the main direction of flow. The physico-chemical dispersion is the molecular dispersion resulting from the chemical potential gradient, which is correlated to

the concentration (Fried et al., 1979, Fried, 1975, Fried and Combarous, 1971). Mathematical models which simulate salt water intrusion through advection only are known as sharp interface models that take into account both the processes of advection and hydrodynamic dispersion are called dispersed-interface transport models(Fried, 1975). In the former it is assumed that the salt water and hot springs water are immiscible fluids separated by a sharp interface, while in the latter a transition zone of mixed salt and hot springs water is considered to be present at the interface (Ataie-Ashtiani et al., 1999).

1.2. Statement of the Problem

Most of the works undertaken (Dindi and Swain, 1988, Tole, 1996, Tole, 1990a, Noor et al., 2011) in the Majimoto area concerning geothermal have come up with a hypothetical model showing the intrusive cutting the area. Concerning geochemistry, only heavy metal concentrations from the hot springs has been undertaken and no work related to the effect of sea water on the hot springs has been undertaken (Tole, 1990a). Lack of information about the effect of sea water on the chemistry of hot springs has impelled the undertaking of this study. In addition to this, there is very little information about the subject of the influence of sea water on the chemistry of the hot springs globally. There is also need to relate the findings with chemistry of hot springs from areas that are free from sea water influence. In this regard, Bogoria hot spring water was used for comparison purposes, to bring out the actual effect of the sea water and bring out the difference between waters influenced by the sea water and rift waters which are free from sea water influence. This would also bring an understanding of how the chemistry of the sea water is affecting equilibration and maturity of the hot springs, a phenomenon that has not been tested in the study area before.

1.3. Literature Review

1.3.1 Majimoto Area

The earliest and most important geological works carried out within the research area appeared in a Geological Survey of Kenya mapping report (Miller, 1952a, Caswell and Baker, 1953, Caswell, 1953b) which described the region as consisting of faulted Permo-Triassic sandstones. The sandstones consist of deltaic arkoses, and fluvial-lacustrine shales, siltstones and sandstones. In their report the researchers concluded that the area is endowed with a variety of minerals

including iron ore, limestone, zinc, zircon, gypsum, manganese, lead, monazite (a calcium phosphate compound), nepheline (potassium sodium and aluminium compound) and gorceite (barium aluminium phosphate compound). Thus there exists a great potential for exploitation of industrial minerals in Kwale district especially on Mrima Hill where several mineral ores such as iron, manganese, niobium, titanium, molybdenum, nepheline and gorceite are known to exist.

Some of the work done previously touching on Majimoto hot springs by assorted researchers (Dindi and Swain, 1988, Tole, 1990a, Tole, 1996, Noor et al., 2011) touched mainly on geology and geophysics and they mentioned the occurrences of geothermal manifestations, and hence this research is providing the first account of the influence of sea water on the chemistry of the hot springs. A series of mineral explorations have been undertaken in the area (Tole, 1990a, Cortec Mining Kenya Ltd, 2012). Other illustrations of precedent works include the reports on The Mineral Exploration in Mombasa Area (Japan International Cooperation Agency, 1991), The Geology of the Mombasa-Kwale Area (Caswell, 1953a) and Geological Survey of Jombo complex and Mrima Hill (Coetze and Edwards, 1959, Caswell, 1953b, Baker, 1953). Other workers include Nyambok (1980) who studied the petrochemistry of the alkaline intrusive in the Jombo hill and (Dindi and Swain, 1988) who conducted a 3-D joint gravity and magnetic inversion which modeled the intrusive to originate from the same magma source.

Work related to geothermal in the area was carried out by Tole (1996), Tole (1996) and Tole (1992) whose results indicated presence of alkaline intrusives of Upper Cretaceous age that outcrop 3-10 km from the hot springs. Monchiquite dykes are associated with two of the three hot springs in the area (Tole, 1990b). Maximum surface discharge temperatures recorded were 56-76°C (Tole, 2003, Tole, 1996). (Tole, 1990a) also conducted a study of heavy metal concentrations in the discharge waters and found presence of Pb, Zn, Cu and Fe. According to this study, it was indicated that massive pyrite was being deposited at or near the surface at three of the hot springs. Although these earlier works noted the presence of Majimoto hot springs, there is no account of any in-depth studies geared towards the assessment of the effect of sea water on the chemistry of the hot springs.

1.3.2 Bogoria Area

As far as Lake Bogoria is concerned, works that touched on geothermal occurrence in the area include the earliest recorded work done by Mohr (1911) who, in his expedition, gave a brief description of the rocks found in parts of the prospect area. Gregory (1896) made further reference to parts of this area in his book of 1921. Prior (1903) described many of Gregory's specimens and Walker (1903) traversed the area from Eldama Ravine to Marigat and from Marigat to Elgeyo Escarpment. In his work, he mentioned presence of agate and opals on the western part of Perkerra River and further mentioned patches of lava at the foot of the Elgeyo Escarpment farther west of the prospect area. This work mainly touched on geological works in the area.

In 1929/30, Bailey Willis (Willis and Willis, 1929) visited East Africa and in his book on the area published in 1936, he discussed the Tugen hills and described the origin of the Kerio Valley and the flanking Elgeyo Escarpment. Fuchs and McInnes (Fuchs, 1950) visited the Bogoria basin and in his book Pleistocene events in the Baringo basin, Kenya Colony and studied the succession within Bogoria basin which showed that the lake deposits are of Middle Pleistocene age. In addition an examination of the relation between these deposits, the volcanic episodes and the periods of faulting, shows that climatic change has not been the major factor responsible for past fluctuations of the lake level.

Detailed geological mapping in this sector of the Kenya rift where the prospect area lie was done in the late 1960s by the Kenya Geological Survey (1960). The Arus and Lake Bogoria areas are included in the regional work of Lake Bogoria focusing on the hot springs, geysers and Holocene stromatolites (McCall, 2010). According to McCall (1967) report "Geology of Nakuru-Lake Hannington area" report was accompanied by two geological maps in the scale of 1:125,000. The western part of the area which partly falls within this prospect area was surveyed by Walsh (1969) and later by Jennings (1971) in the "Geology of the Eldama Ravine & Kabarnet area" report which was accompanied by a geological map in the scale of 1:125,000. In their work, they gave detailed description of the volcanic rocks and the sediments and were able to draw up a fairly detailed history of the tectonism. They also gave a detailed description of the surface manifestations found in the area between Arus and Lake Bogoria.

Glover (1972) collected a large number of water and steam samples from Lake Bogoria area and concluded from his analytical data that a relatively large and homogeneous body of warm water lies under much of the area.

Griffiths and Gibson (1980) in their work, which focused on the geology and petrology of the area. In their findings, a large number of flows were erupted from widely dispersed centers to form an extensive volcanic shield within the floor of the rift. They further noted that the major element composition of most rocks was substantially modified during crystallization.

Geological work in the area with bias in geothermal exploration was carried out by Italiana (1987). In their report covering Menengai-Bogoria reconnaissance work, they did some geothermal exploration, which dwelt mainly on Menengai caldera but did not discuss geological and structural setup for development of the extensive anomalous geothermal manifestations in the area to the north.

Tiercelin et al. (1987) did some multi-disciplinary investigations on the distribution in space and time of the sedimentary and biogenic facies in the Baringo-Bogoria half graben based on the study of outcrops and cores 0.5-18 m deep. They defined the recent environmental conditions and indicated that, despite identical context structure, climate and vegetation, the two lakes show completely different mineral and organic sedimentation with Lake Baringo being a holomictic fresh-water lake and Lake Bogoria a saline -alkaline lake with a meromictic regime and a high hydrothermal activity.

1.4. Objectives

The general objective of this study is to use thermal fluids from Majimoto and sea water to evaluate the effects of sea water on the chemistry of hot springs with comparison to Bogoria hot spring waters. The specific objectives are as follows;

1. Assess the type of hot springs waters and how the sea water has influenced this chemistry. Including determining the proportion of sea water in Majimoto springs and investigating the progressive changes in the chemistry of the Majimoto hot springs away from the sea water located 18kms to the North of Indian Ocean.

2. Ascertain the influence of sea water on the maturity and equilibration of the Majimoto hot springs with comparison to the Bogoria hot spring waters.
3. Investigate and illustrate the mixing scenarios that may be present between the sea water and Majimoto hot springs.

1.5. Justification of Research

The three Majimoto hot springs located about 18 kms north of the Kenyan south coast, are believed to be most likely being controlled by an underground intrusive hot body (Dindi and Swain, 1988; Noor et al., 2011, Tole, 1990b, Tole, 1992, Tole, 2003). Tole (1990b) in their findings, they found out the presence of alkaline intrusives of Upper Cretaceous age that outcrop 3-10 km from the hot springs. Monchiquite dykes are associated with two of the three hot springs in the area. Maximum surface discharge temperatures recorded were 56-76°C (Table 4.1). The waters are dilute, near neutral to, slightly alkaline pH fluids, with a fairly high Mg concentration. Tole (1992), suggested a common origin of the waters for the three Majimoto springs but further recommended further work to prove this conclusively.

The research seeks to assess the type of hot spring water from Majimoto and find out how the sea water has changed its chemistry. It would be important to find out if there exists a relationship between the Majimoto hot springs and the sea water. If a relationship exists it would be important to find out the proportion of the sea water that is present in the hot spring water. In addition to this it would be important to know how progressively the chemistry of the hot springs has changed. This would be achieved by comparison with the compositions of Bogoria waters and composition of waters expected from equilibrium with an isochemically recrystallized, thermodynamically stable average crustal rock. Knowledge about these assessments would be beneficial in recognizing the type of water the hot springs are emanating, if the waters have a sea water component and in what proportion and how progressively have the waters changed from the sea water. This basically seeks to undertake the initial assessment of the water from the hot springs.

In ascertaining the influence the sea water on the maturity and equilibration of the Majimoto hot springs, the research seeks to find out how the sea water has influenced the interaction of the hot spring water with the surrounding rocks on its way to the surface. Maturity of geothermal

waters can either be affected by sea water or groundwater. Maturity of the hot spring water determines whether the calculated geothermometry temperatures will be reliable or not. This is quite important because out of every hot spring in a geothermal prospect everybody wants to know the temperatures at the reservoir.

By investigating and illustrating mixing scenarios occurring between the sea water and the Majimoto hot springs, the research seeks to find out the path of mixing that the Majimoto and the Bogoria hot springs follow. This will seek to give light to what are the main cause low and elevated chloride and find out where the mixing is leading to.

1.6. Significance of Research

This study will focus on evaluating the geochemical characteristics of Majimoto hot springs and Bogoria hot springs in the quest of assessing the effect of sea water to the chemistry of the hot springs. In principle it would be of great significance in understanding how sea water can influence the chemistry of hot springs a subject that is not well researched all over the world. Many hot springs all over the world are found in the vicinity of hydrothermal systems in volcanic areas. A common way has been developed on how these hot springs can be assessed and interpreted and none of the ways i.e. geothermometry are applicable to hot springs found in sedimentary environments i.e. in epithermal systems. In this regard, the findings of this project will be vital in producing a new way of interpreting hot springs found in sedimentary systems close to the sea water whereby the proportion of sea water has to be removed from its chemistry first before interpretation is done. The results of this project are also important in meeting the above-mentioned objectives in search of understanding and improving knowledge on the little studied subject of the influence of sea water in hot springs found within sedimentary settings.

Chapter 2

2. Study Area

2.1. Location and Description of Majimoto hotsprings

Majimoto hotsprings are located at the Kenyan South Coast in Kwale district (Figure 2.1). The hotsprings lie at the immediate north of Mrima-Dzombo Hill. The hotsprings are distributed within an area of approximately 6 km². The hotsprings are also characterized by *Fimbristylis exilis* -geothermal grass

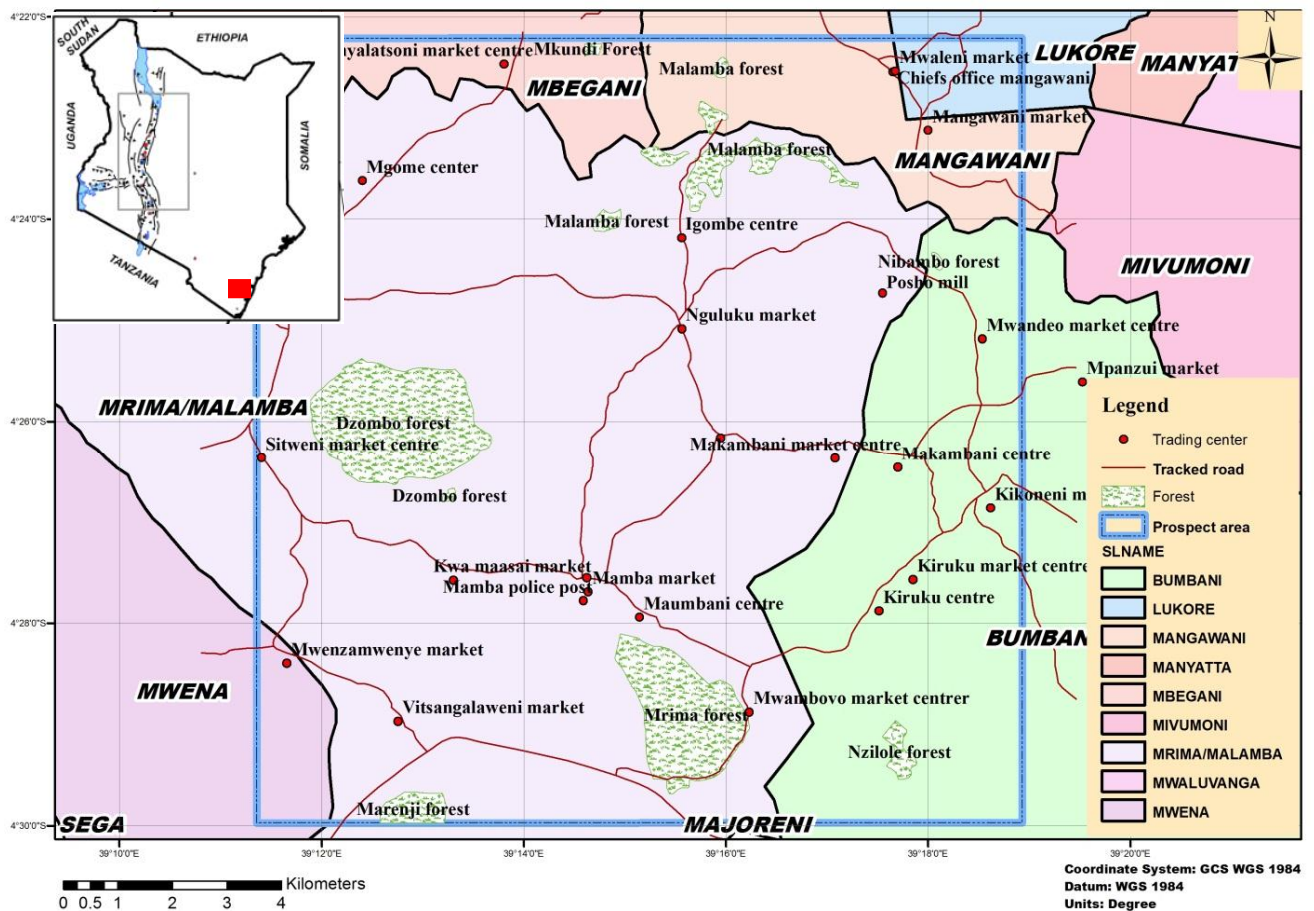


Figure 2.1: Location of the study area

The area surrounding the hotsprings is generally faulted and the rocks are mainly dominated by Permo-Triassic sandstones. The hot springs discharge slightly alkaline NaCl NaHCO₃ waters from underground, suggesting the springs are most likely being controlled underneath by an

intrusive hot body. The host rock is Mariakani sandstone which is weathered and sheared. It is overlain by red concretions of iron, manganese and niobium which are considered radioactive elements. They are extruded by carbonatites forming the vent at the top of the hill. The main ecosystem type in the study area is forest, the Mrima Hill itself, and the surrounding cropland. The closest arm of the sea, a mangrove lined shallow creek, comes within 18 km of the Majimoto hot springs.

2.1.1. Geology and Structures

The general geology of the area chiefly consists of the sediments of Triassic to Jurassic ages, igneous rocks of Cretaceous age and the unconsolidated sediments of Tertiary to Quaternary ages (Gregory, 1921, Miller, 1952a)(Figure 2.2). Triassic to Jurassic sediments are chiefly comprised of sandstone beds. Igneous rocks are widely observed in the form of intrusive rocks of varied type. Unconsolidated sediments are observed to be of Tertiary sediments and of colluvial, residual and alluvial sediments of Quaternary age. In summary, rocks in this area are largely of sedimentary origin and range in age from Permian (or possibly Upper Carboniferous) to Recent. Three well-marked divisions can be recognized (Gregory, 1921, Miller, 1952a);

1. The Cenozoic Rocks.
2. The Upper Mesozoic Rocks.
3. The Duruma Sandstone Series.

The Duruma Sandstone Series is a correlative of the Karoo System of South and Central Africa consists of grits, sandstone and shales. The series is divisible into three broad lithological units with coarse sandstones and grit at the top and bottom of the succession, and finer sandstones and shales in the middle. These beds were mostly deposited under lacustrine or sub-aerial conditions, with materials having been derived from the Basement System rocks. The Upper Mesozoic rocks are stratigraphically unconformable upon the Duruma Sandstones but their contact is highly faulted (Gregory, 1921, Miller, 1952a).

The Cenozoic (Quaternary & Tertiary) rocks rests unconformably upon an eroded surface of Mesozoic rocks with occasional overlap on to the Duruma Sandstones. Alkaline igneous intrusions at Dzombo Hill, where nepheline-syenites, ijolites and melteigites outcrop, and associated vent agglomerates and dykes are the only eruptive rocks of the area. The intrusions

and volcanic activity associated with them have been referred to the Cretaceous or Tertiary (Gregory, 1921, Miller, 1952a).

The general geological structure of Mesozoic sediments in the area is interpreted to show ESE-WNW to ENE-WSW trending with gentle dipping towards north-western part of the area, while, NNE to SSW trending with gentle dipping toward east in eastern part (Gregory, 1921). A slight increase in the angle of dips is observed near the junction of the Mariakani Sandstones and reversed dips at Ramisi River to the north of Dzombo Hill, along the eastern flanks of Shimba Hills and in the topmost horizons of the Jurassic and Cretaceous rocks. In each case, the reversed dips appear to be accompanied by minor faulting immediately to the east, and it is possible that the relief of stress caused a slight marginal tilting of the strata on the up throw side. The Cenozoic rocks are all more or less flat-lying and undisturbed by faulting. Two types of faults, ESE to WNW and ENE to WSW directional, which show an accordant representation with lineaments, are developed in the area. A lamprophyric dyke shows such trends, as N60•W, N75•W and N40•E, which are also directionally accordant mostly with faults and lineaments (Gregory, 1921, Miller, 1952a).

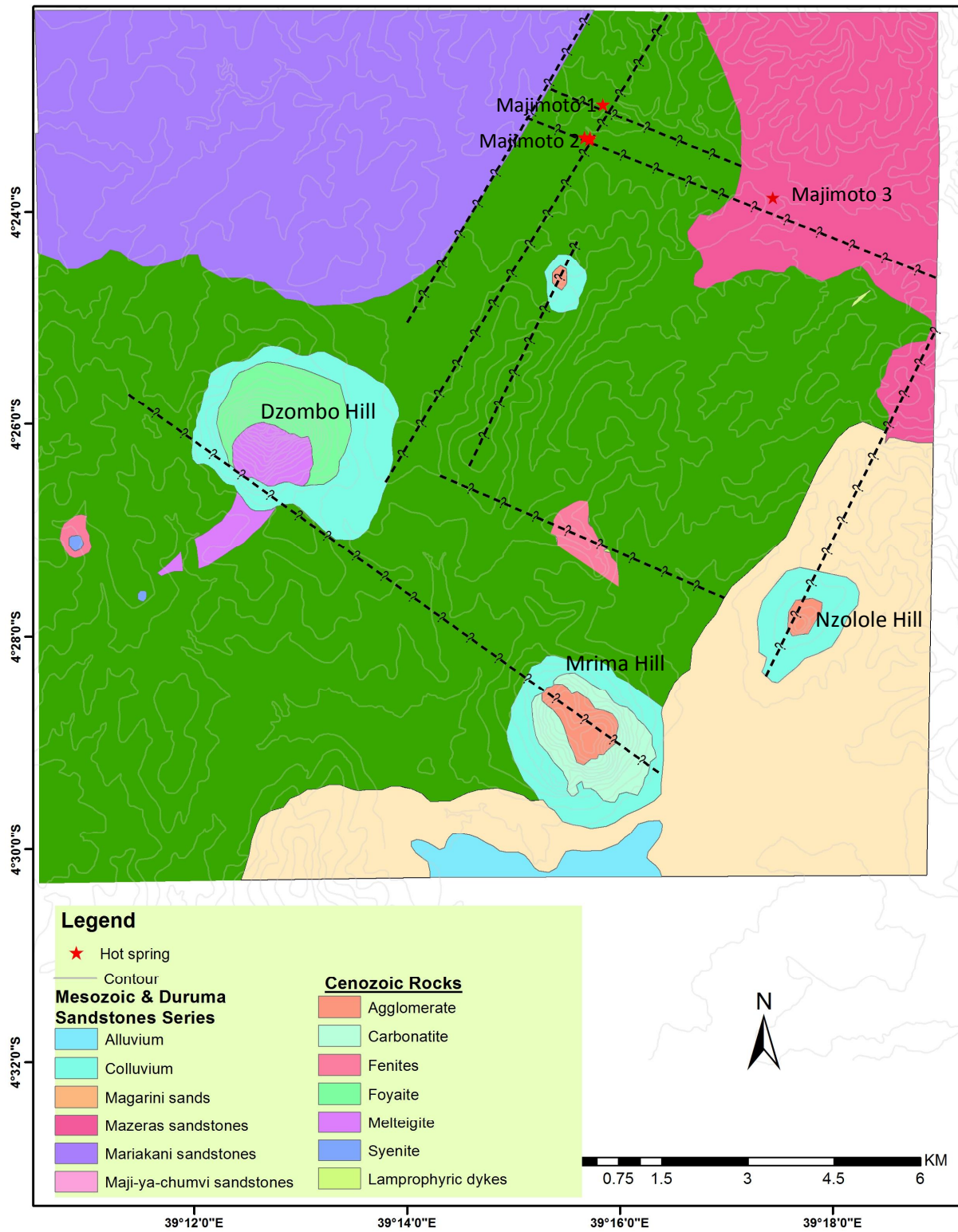


Figure 2.2: Geological map of the Majimoto area(Modified from Gregory (1921)).

2.1.2. Thermal Areas in Majimoto

The thermal activity in study area occurs in three main areas (Figure 2.3). Majimoto 1 and Majimoto 2 hotspots occur in close proximity while Majimoto 3 occurs to the east of project area.

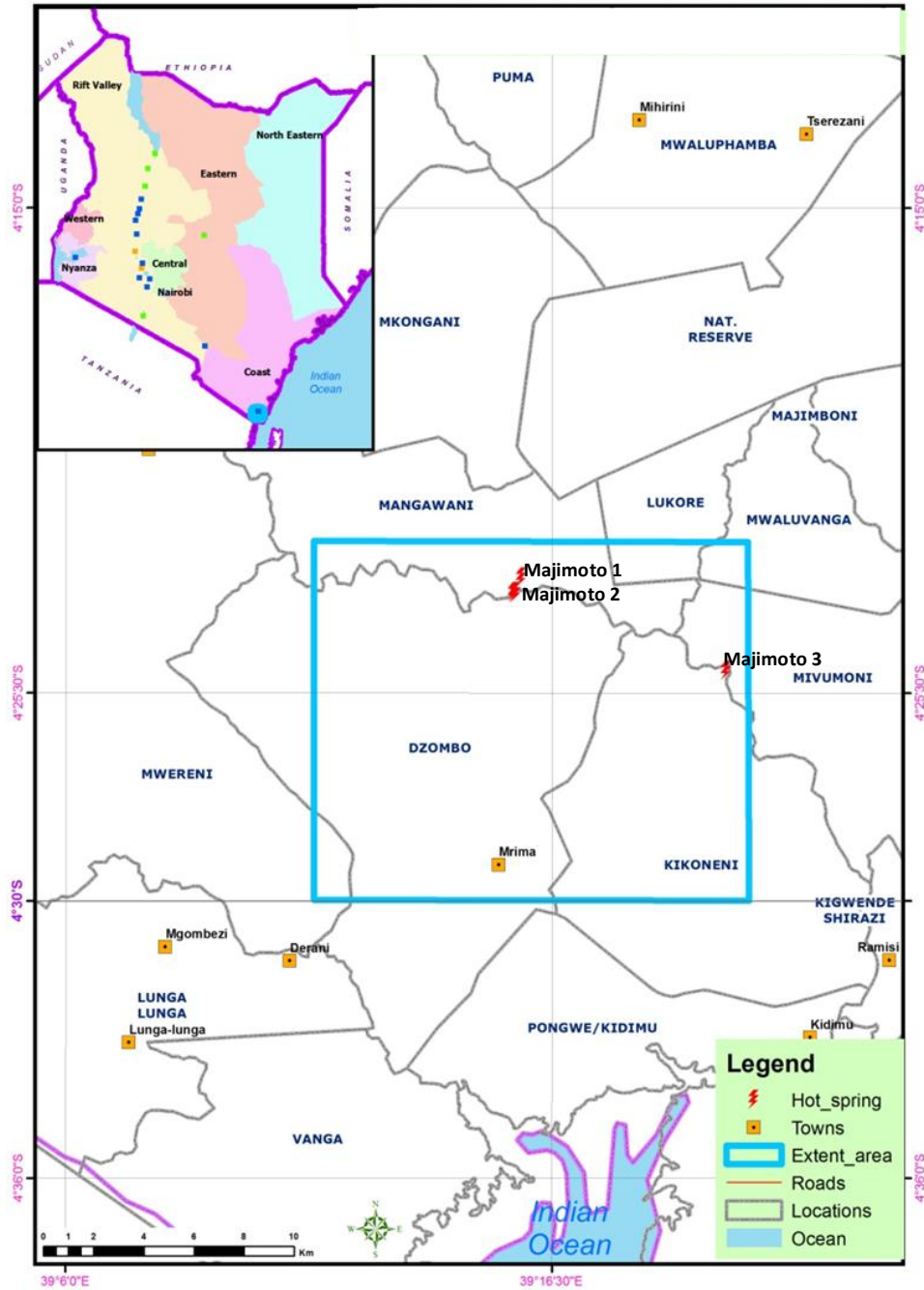


Figure 2.3: Map showing the location of the hotspots within the study area

Majimoto springs are not associated with high temperature geothermal activity such as fumaroles and altered ground. The thermal springs are found in a sedimentary formation with intruding igneous dykes. The estimated total flow from natural springs is estimated at 90 liters/second and the spring discharge temperatures range from 55 to 70°C. Location of the hot springs is oriented in a NE-SW direction (Figure 2.3).

2.1.3. Climatic Setting

Msambweni district has monsoon type of climate characterized as hot and dry from January to April and cool between the periods June to August. Rainfall is bimodal with short rains experienced from October to December whilst the long rains are experienced from March/April to July. Total precipitation varies between 900mm - 1500 mm per annum (Jaetzold and Schmidt, 1982, National Coordination Agency for Population and Development, 2005). Data from a sample station in Kwale monitored between the years 2000 - 2009 recorded an average annual rainfall of 657 mm (Ministry of State for Development of Northern Kenya and Other Arid Lands, 2010). This is a markedly noted decrease in the average annual rainfall intensity to the North and the hinterland. Mwaluphamba and Mkongani Locations of Kubo division (Majimoto prospect) and Golini and Tsimba Location of Matuga Division have demonstrated a high rainfall pattern with fairly dense drainage due to run off from the hills (National Coordination Agency for Population and Development, 2005).

2.1.4. Vegetation

The area is endowed with very rich biodiversity in terms of vegetation ranging from herbs, shrubs and trees (Moomaw, 1960). Natural vegetation is dominated by the woody vegetation of the palmar family and include *Cocos nucifera* (coconut palm), *Hyphaenecompressa* (doum palm), *Adansoniadigitata* (Baobab tree), *Mangifera Indica* (Mango Tree), *Acacia spp*, *Thevetiaperuviana*, *Terminaliacattapa*, *Makharmialutea*, *Casuarinaequisetifolia*, *Euphorbia candelabrum*, *Sterculiaappendiculata* (Mfuno), *Artocarpusheterophyllus* (Mfenesi) and *Miliciaexcelsa* (Mvule), *Eucalyptus spp*, *Alpinaarundinaria* (Mountain bamboo), *Croton megalocarpus*, *Spathodeanilotica* (Nandi flame), *Grevillearobusta* (Silk oak), *Ceibapentandra* (Msufi), *Solanumincanum* and *Lantana camara* among others (Moomaw, 1960, Glover et al., 1969). Virtually all the above species are found on farms and in the forest specifically the

Dzombo and Mrima forest. The prospect also has a rare tree species namely *Mimusopssomaliensis*. Other endangered tree species include *Melicia excels* (hard wood) and the precious timber tree *Brachillienahullensii*; (ፋጠህህግግ)(Glover et al., 1969). The noted common fauna in the area include rodents such as the garden mouse and porcupine, dikdiks, monkeys and baboons while avifauna included both forest birds such as the Lilac breasted roller, cattle, egrets and Common drongo and birds of prey such as the African harrier hawk eagle. The Dzombo and Mrima forests are Important Bird Areas (IBAs) rich in avifauna, with 35 forest-dependent species recorded(UNCRD et al., 2011).

2.1.5. Land Use and Land Resources

Msambweni district, the location of the geothermal manifestations is endowed with a number of forests and mainly Mrima and Dzombo. Dzombo forest Reserve is considered as a protected and sacred area by the local community (Waiyaki, 1995, Waiyaki and Bennun, 2000).The local community has been very active to issues concerning conservation. Many conservation groups have also been established. These groups are involved in seedling production, forest policing, rehabilitation of degraded areas and sustainable forest produce usage. Key conservatory efforts noted include; enrichment planting within the forests; rehabilitation of the degraded sites; nursery establishment and management; awareness creation on the importance of the existing forests; on farm trees planting by establishment of woodlots; participatory forest management; forest policing by the Kenya Forest Service (KFS); development of forest management plans for various forest pockets within the zone; formation of Community Forest Associations (CFAs); and enforcement of the charcoal rules which involves the formation of the Charcoal Production Associations (CPAs).

2.1.6. Agricultural Activities

The area is classified as lowland in terms of agro-ecological zones with little rainfall and high temperatures(Jaetzold and Schmidt, 1982). It lies within Agro Ecological Zones III and VI and supports livestock production and subsistence agriculture. Msambweni district has a high potential for agriculture and livestock production. These form a majority of the households. About 70% of the total land area is arable with only 40% under cultivation. Farmlands are located near residential areas with average smallholder farm sizes ranging between 2 and 10

acres, and commercial large scale farms at 100 acres. The farmers still practice noncommercial agriculture preferring low input systems of production. Msambweni district remains food deficit for approximately six months in a year with large amounts of money spent annually to buy food outside the district due to underutilization of crop production potential (Jaetzold and Schmidt, 1982). Livelihoods in Msambweni district are mainly dependent on agriculture. Major crops produced in the division include maize, rice, cowpeas, beans, pigeon peas, sweet potatoes and cassava for food while coconuts, cashew nuts, mangoes, sugarcane and citrus fruits are grown as cash crops among others. The district has already started implementing the Farmer Field Schools (FFS), a focal area extension approach to transfer technology to farmers.

2.1.7. Natural Resources

The district is endowed with a lot of natural resources e.g. forests (Mrima-376.8 Ha; and Dzombo -906.5 Ha) with rich biodiversity and sand among others. There exists a great potential for exploitation of industrial minerals in the district especially in Mrima Hill where several minerals such as iron, manganese, niobium, titanium, molybdenum, nepheline and gorcita are known to exist. Preliminary estimates of manganese ore reserves at Mrima Hill place the tonnage at over six hundred thousand (600,000) while the tonnage of iron ore is estimated to be between three and fifteen million (3,000,000-15,000,000) (Cortec Mining Kenya Ltd, 2012, Abuodha, 2002)

2.1.8. Physiography

Dzombo hill is the highest peak in the area and rises to a height of 477 m above the sea level, 300 m above the average level of the surrounding plain. It is of sub-conical shape with a summit ridge running in an east-west direction (Figure 2.4). The upper slopes are covered by dense forest and undergrowth which extend down to the base on the western, northern and eastern sides. Mrima hill lies 8 km S.E. of Dzombo. It is a broad dome-shaped hill that attains an altitude of 265m asl. Mrima hill has in the past attracted attention by virtue of the manganese laterites that cover its surface. Like Dzombo hill, Mrima is covered by dense vegetation. Exposures are few owing to a thick layer of distinctive red-brown soil caused by the weathering of the manganese and iron ores. Kiruku hill, lying 4.5 km N.E of the Mrima, is conical in shape rising to 180 m asl and is also covered by thick vegetation. Ngulukuku hill also has a conical outline and is

situated 6 km N.E of Dzombo at 168m asl. The surrounding area is flat-lying with infrequent broad shallow valleys that often form valleys in their lower parts. The soils are brown and sandy except in the more poorly drained areas where they are of -black cotton type. The plain is well-grassed and covered with thorn trees and thick clumps of bush.

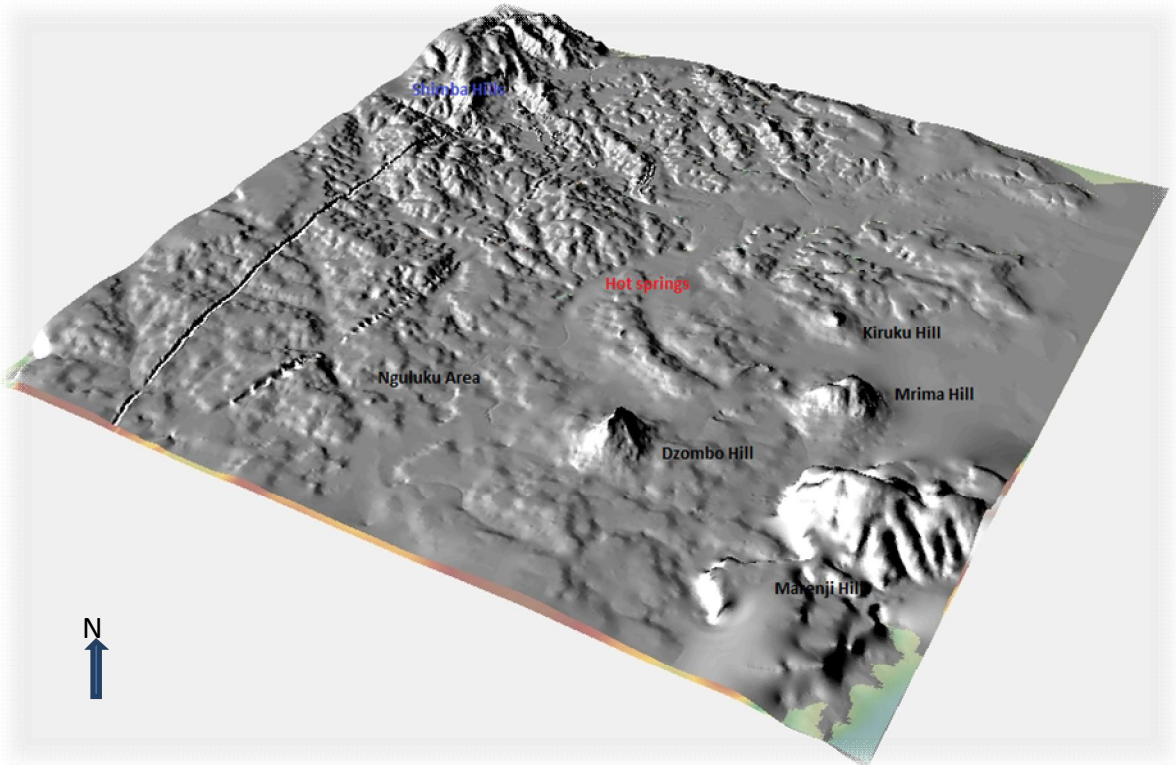


Figure 2.4: A 3-D relief map showing the physiography of the study area

2.1.9. Drainage

The drainage in Majimoto area is strongly controlled by the structural elements of the region. Surficial drainage drains radially away from raised grounds following valleys, faults or fissures zones (Figure 2.5). The dominant water body in the proximity of the prospect is the Indian Ocean which is approximately 8.5 km away. River Ramisi is the major river with Rivers Chorochoro, Ndzovu and Sadani as the major tributaries. The major sources of water for domestic use are boreholes, shallow wells and water pans. Aquifer depths in water-point boreholes and wells in the entire prospect area indicate huge volume of shallow hydrogeological regime. Fresh waters exist at a maximum depth of 50 m beyond which saline water exists. Saline water at deeper depth could be as a result of mixing of ocean waters with underground water.

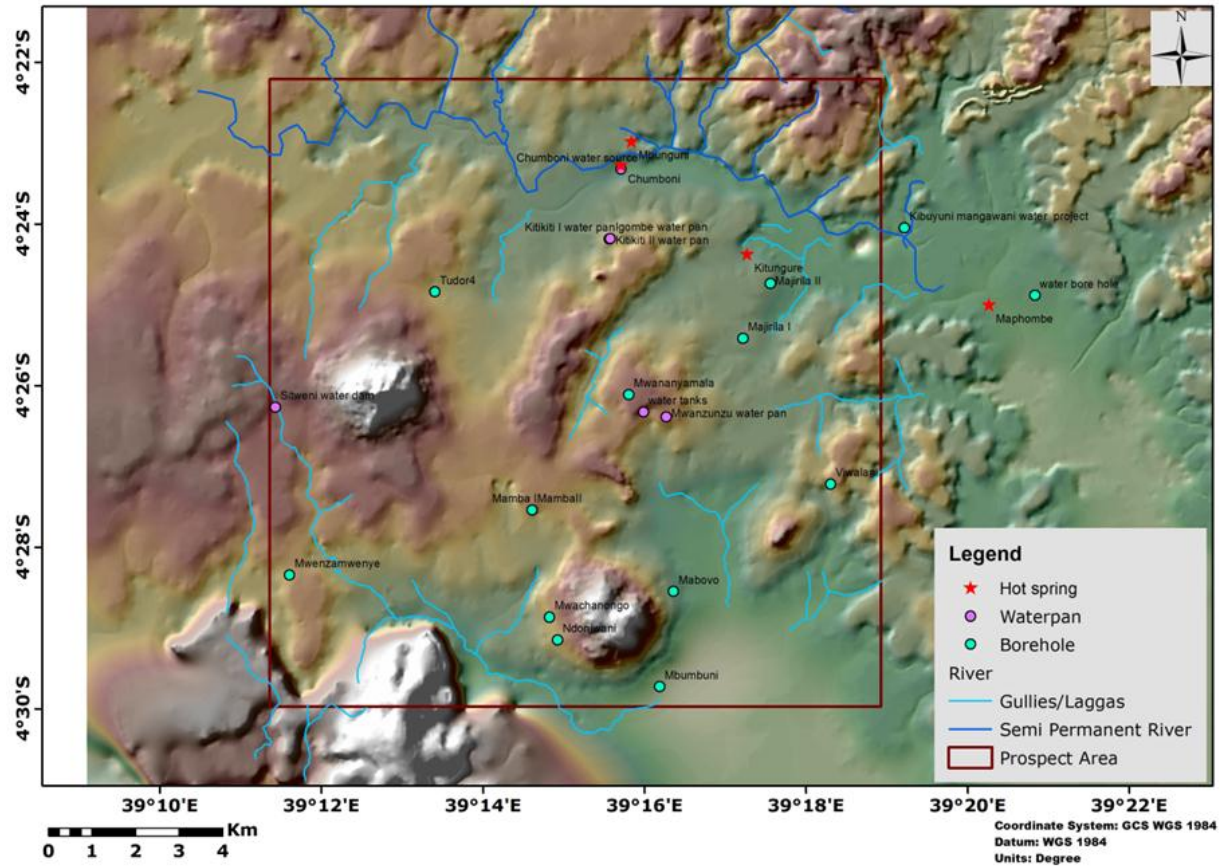


Figure 2.5: A DEM map showing the drainage systems of Majimoto area.

The deep subsurface groundwaters in the prospect appear to follow deep geological structures within the inferred weak zones, which are caused by lately occurred igneous intrusions in the earlier sedimentary deposits.

These groundwater hydrogeological regimes are widely believed to be emanating from the north western lying ranges of Shimba hills. These groundwaters are believed to be getting mixed up with ocean waters and percolate through deep-seated fractures and get into contact with hot intrusive dykes north of the massive Dzombo hill extrusion (Tole, 2003). The waters are heated up then rise up to the surface to form hot springs at Majimoto area.

2.2. Location and Description of Bogoria

The Bogoria hot springs within the Lake Bogoria geothermal prospect (LBGP) are located within the eastern floor of the Kenya rift valley (Figure 2.6).

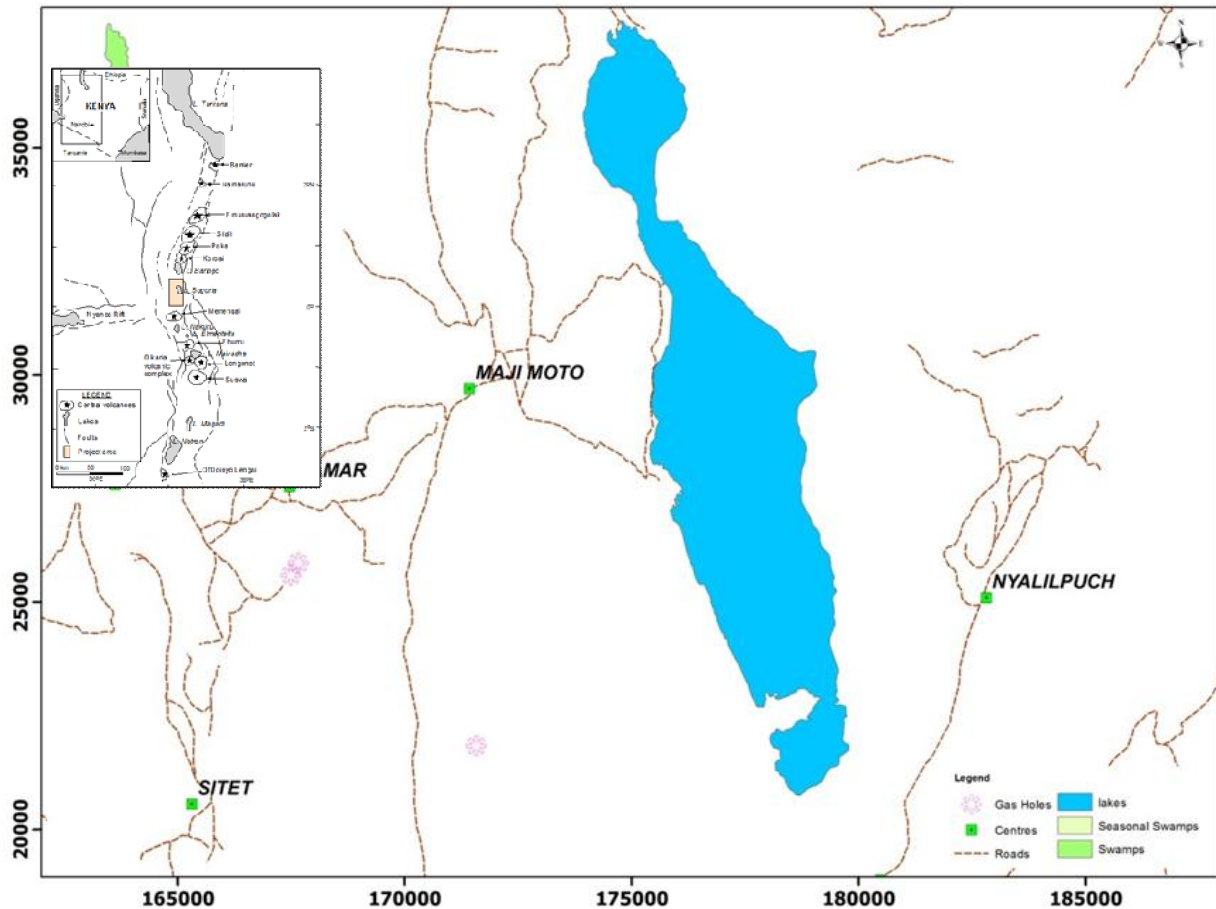


Figure 2.6: Location of Lake Bogoria thermal springs

The LBGP is bound by latitudes 20000 N and 35000 N and longitudes 165000 E and 185000 E within the rift graben (Mulwa and Mariita, 2013). Lake Bogoria is a prominent feature occupying part of the Bogoria prospect. The current study covered an area of approximately 2000 sq. km (Figure 6). The Lake Bogoria prospect encompasses several features of geological significance that are considered indicators of possible geothermal potential.

2.2.1. Geology and Structures

The upper Plio-Pleistocene volcanism of the rift floor in the area between Arus and Lake Bogoria is characterized by large volumes of evolved lavas that consist mostly of peralkaline trachyte, trachy-phonolites and phonolite (McCall, 1967, Walsh, 1969, Dunkley et al., 1994). Small outcrops of basaltic lavas occur in isolated areas within the prospect. The northern sector is, however, dominated by fluvial and alluvial deposits. The geological map showing all the outcrops encountered in the area is presented in Figure 2.7. The main structural features in the

Arus and Lake Bogoria areas include; the eastern rift flank, the rift proper, NW, NNE and N-S trending faults and fractures and the Marigat and Lobo lineaments (Figure 2.7). The most prominent of the NW trending faults is the line of Sattima-Aberdares and Marmanet Faults. Its complement to the north comprising the Lariak-North Arabel and other shorter minor faults forms a belt of discontinuous fractures (Walsh, 1969, Dunkley et al., 1994). Progressively towards the northwest, both fault zones display an *en echelon* displacement to the west. The NNE trending faults form a dense swarm of 8-10 km, which correspond, generally to much of the eastern shoulder of the rift. In the north the margin of these NNE trending faults, is clearly demarcated by Laikipia Monocline clearly defined by dip variations (1-2km) and the Loriki Escarpment (Dunkley et al., 1994) (Figure 2.7). To the south interaction with faults trending N-S and NW-SE enhances the composite effect of sigmoidal elements, which contribute to the flexure in the rift structure south of Lake Bogoria. Faults trending N-S are fractures with a broadly meridional trend which tend to interact with the NNE trending faults in the eastern rift shoulder (Walsh, 1969, Dunkley et al., 1994). These faults are the dominant structural elements of the rift floor and are notably the grid-faulted platform west of Lake Bogoria and the fissure system. The same structures are aligned to the vents and the cinder cones of Korosi and Paka volcanoes further north of the prospect area (Dunkley et al., 1994).

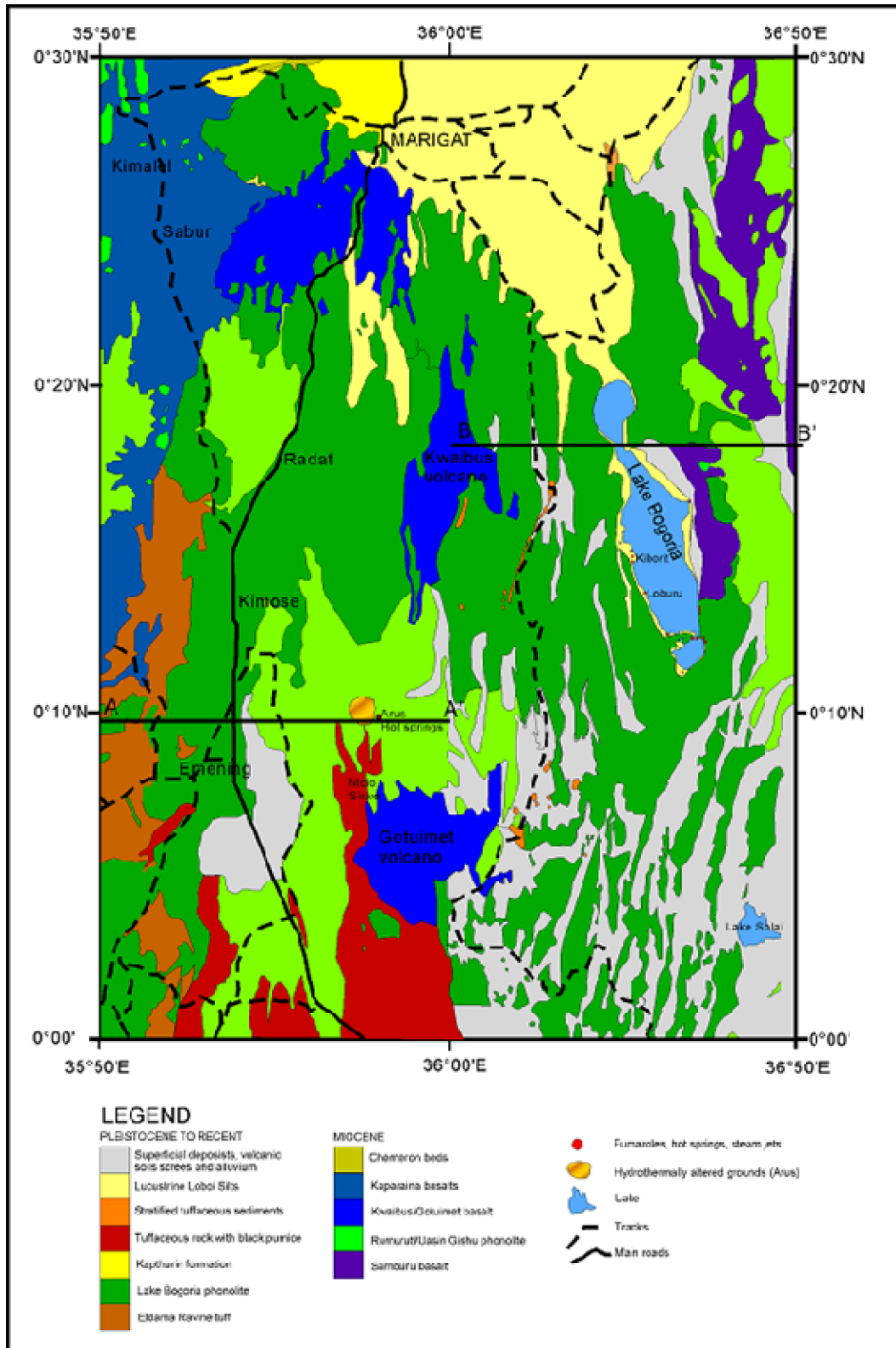


Figure 2.7: Geological map of the Arus and Lake Bogoria geothermal prospects. Modified from Walsh (1969) and McCall (1967)

The NW trending faults, which comprise the Sattima-Aberdares and Marmanet Faults, coincide with the major NW shear zones, which are considered to reflect reactivation of the Precambrian Mozambiquan belt formation (Walsh, 1969, Dunkley et al., 1994). The important structures are the Ol-Arabel and Lobo/Marmanet lineaments (Figure 2.7). The interaction between these faults and the NNE ones has created an intensely sheared/fractured zone to the northeast of Lake Bogoria at the Laikipia Escarpment. The shearing has caused some of the Lake Bogoria phonolites to develop fissility (slaty) texture, which trend in the same direction (Walsh, 1969, Dunkley et al., 1994).

2.2.2. Thermal Areas of Bogoria

The major thermal manifestations within this area include geysers, hot springs and fumaroles which can be observed along the shores of the lake with temperatures ranging from 85-98°C (Karingithi and Wambugu, 2008). Figure 2.8 below indicates the location of the fumaroles that would be used in this study.

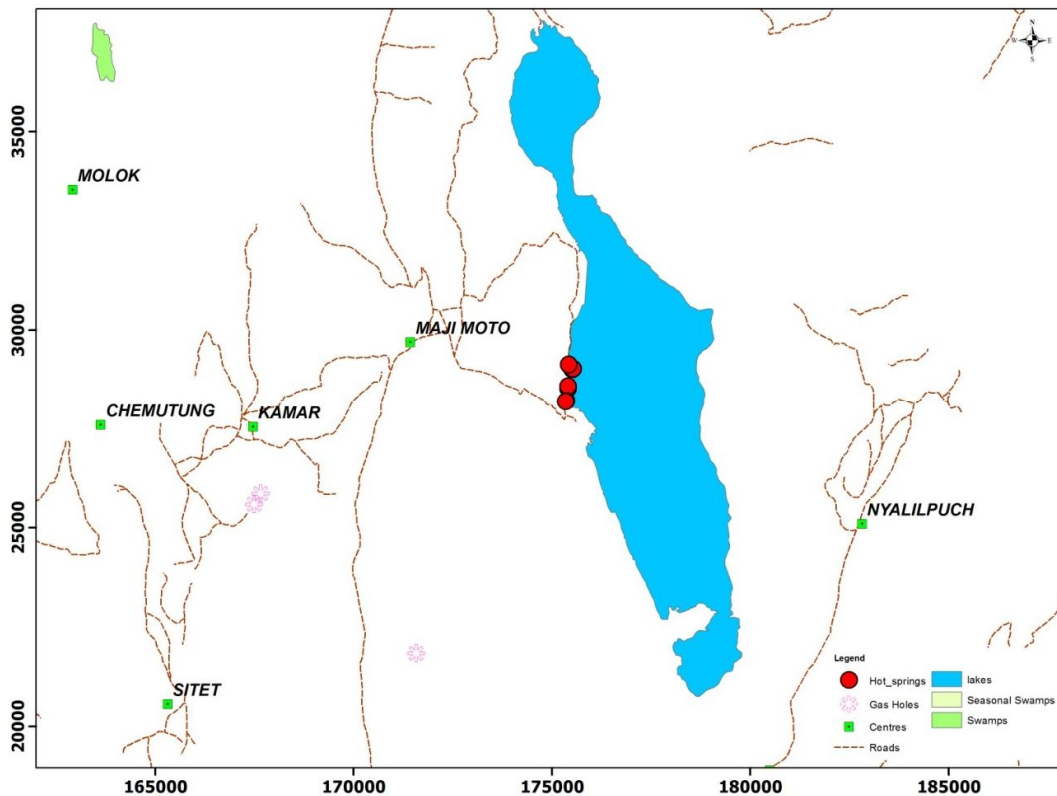


Figure 2.8: Map showing the location of the hot springs within Bogoria study area. Compiled from results of the present study

2.2.3. Climate

The climate in the study area is arid to semi-arid regimes except in the moist highlands around Subukia. The climatic conditions are strongly influenced by the ITCZ (Inter Tropical Convergence Zone) and there are two distinct wet and dry seasons. Within the reserve and adjacent areas, the climatic conditions are harsh with temperatures at the Lake ranging from 18°C-39°C with a daily mean of 25°C (Harper et al., 2003, Wetangula et al., 2010). Mean annual precipitation varies from 500-1000mm and falls in two seasons April - May and October to November. The physiographic location of the reserve in a graben places it in the rain shadow of the surrounding fault scarps and highlands. The combination of weather variables and physiographic location give the lake basin a hot, semi-arid climate (Harper et al., 2003, Renault and Owen, 2005, Wetangula et al., 2010).

Lake Bogoria and its surroundings are categorized under agro-ecological climatic zone E. Rainfall reliability is low (Mwangi and Swallow, 2008), and daily sunshine hours average 10 making the area hot for most of the year (Krienitz et al., 2003). There is a marked hot spell from January to March when temperatures in excess of 34°C are experienced. Cold spells occur in the months of July and August.

2.2.4. Drainage

The drainage pattern in and around Arus and Lake Bogoria prospect area is shown in Figure 2.9. The Perkerra River, which drains the Mau Escarpment west of Eldama Ravine and Tugen hills, is the largest river in the prospect. Its flow dwindles east of Marigat and north of Logumkum and disappears into the Oloi Matashu swamp and only recharges Lake Baringo, which is north of the prospect area from subsurface flows. The Molo River that is also a permanent stream drains the Mau Hills near Molo and Elburgon. It tapers on reaching the floor of the rift valley and similarly recharges Lake Baringo via subsurface flows.

The Ndolaita River is a smaller stream than the Molo and Perkerra rivers. It drains the area west of Lake Bogoria. It is an intermittent stream and hot springs at Ndolaita provides an additional source although not significant. The Ndolaita River loses its identity into the Loboï swamp appearing in the north following a well-defined course joining the Molo River in the Ngarua

swamp, near Logumkum. Hot springs west of Loboï and at Lake Bogoria hotel provide a permanent flow draining into the Loboï swamp.

Rivers Iguamiti and Subukia and many other tributaries from the Laikipia escarpment and at Bechot plateau combine to form the Wasagess River, which then drains into Lake Bogoria. This river is seasonal. Other small rivers feeding Lake Bogoria include Emsos at the south and Ngiriki, Parkirichai, Sokal and Kipsirian at the west.

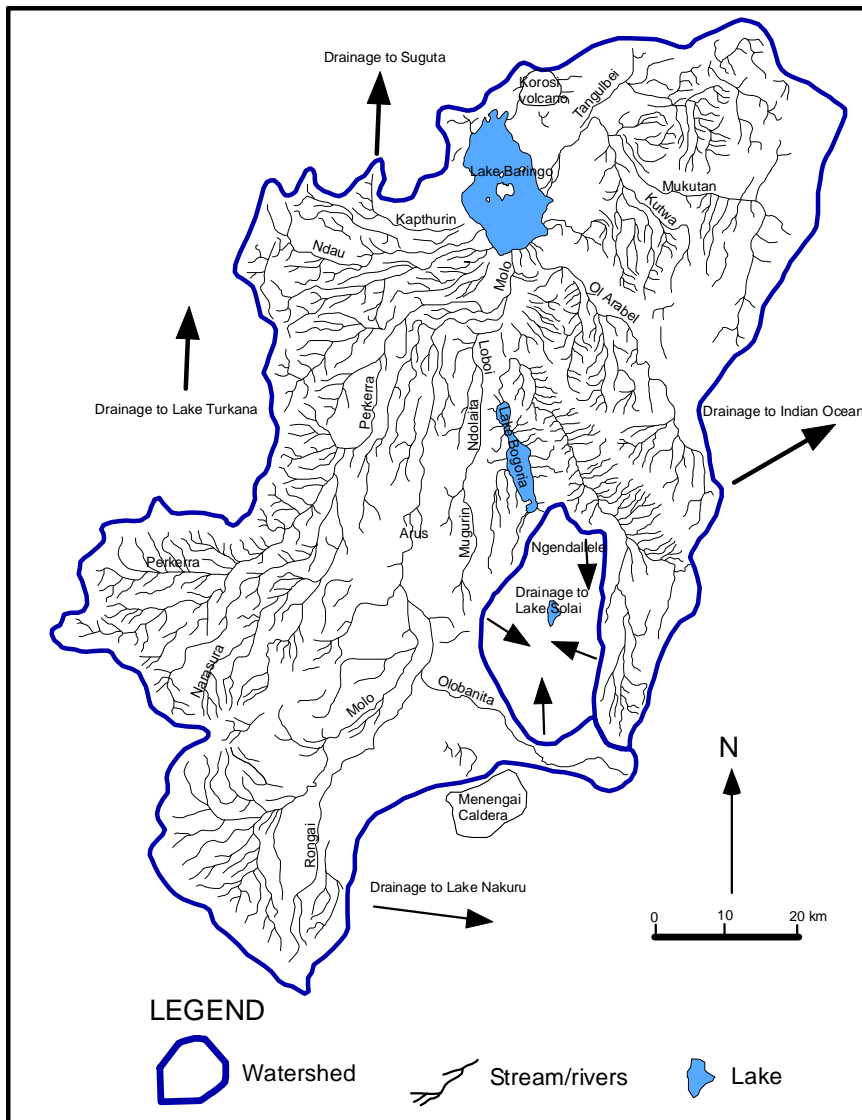


Figure 2.9: The map of the regional drainage system in the Arus and Lake Bogoria geothermal prospects (Modified from Tiercelin and Lezzar, 2004)

2.2.5. Vegetation

Within the reserve, biodiversity inventories have identified approximately 210 plant species belonging to 53 plant families in the reserve and neighbouring wetlands. Amongst these, are 38 species of *Graminae* and 15 of *Acanthaceae*. These species are distributed in six broad vegetation types (Mwangi and Swallow, 2008). These are; riverine forests, wooded bush land, bushed thicket, bush land, bushed grassland and swamps. These are further classified into ten vegetation communities on the basis of dominance. Dominant grasses include *Sporobolusiocladus*, *Dactyloctenium aegyptium*, *Chlonisvirgata* and *Digitariavelutina*. Shrubs include *Grewiatenax*, *G. bicolor*, *Acalyphafruticosa* and *Acacia mellifera*. The most dominant tree species is *Acacia tortilis*. Other community types include mixtures of *Balanitesaegyptica*, *Combretum spp.*, *Ficus spp.*, and *Terminaliaspp* and semi deciduous bush land cover large areas along stream valley and other inhospitable areas.

The area is rich in wildlife species which form part of the fauna. Animals found in the study area include the Greater Kudu etc. There are several reptiles that include monitor lizard, lizards, tortoise, crocodiles and various species of snakes. The lake holds huge congregations of lesser flamingo that feed on the high production of blue-green algae dominated by *Spirulinaplatensis*.

2.2.6. Land Tenure System

In terms of land holding system, most of the lands in the prospect area is communal land (trust lands) but land adjudication is on-going to facilitate private ownership. Land adjudication and surveying is on-going and several land adjudication sections have been established and include Maji Ndege area (Loboi, Mbechot, and Kapkuikui villages), Maji Moto, Koitumet, Cheparandi (Emining) and Wasseges (Kisanana) adjudication sections(Mwasi, 2004). In Mogotio Division, much of the land is under sisal farming under private ownership. No livestock group ranches exist in the prospect area. Currently, no map regarding land ownership is in place as land registration is still in progress(Mwasi, 2004).

2.2.7. Agricultural Activities

Demographic changes have led to changes in lifestyle influencing land use patterns in terms of agricultural activities, where agricultural activities and pastoralism are practiced in fragile

habitats. This has been aggravated by the shift to individual landholding, reduced communal grazing and changes in settlement patterns.

2.2.8. Natural Resources

Ruby deposits have been discovered at Kaplengoi and Kurintoi in Mochongoi division. The current prospecting site is East of Lake Bogoria around Mbechot area and West of Marigat. Corby Company Ltd has been issued with prospecting licenses for three areas at Mbechot in Mochongoi Division. Trona deposits on the shores of L. Bogoria are mined on a small scale by pastoralist community for their livestock.

Chapter 3

3. Methodology

3.1. Materials and Methodology

The methods used in this study are based on the objectives of the study as given in chapter 1. The characteristics of the sea water that are considered vital to affect the hotsprings chemistry were considered in this study. The arrangement of the primary stages and the activities under them are presented by the flowchart in Figure 3.1.

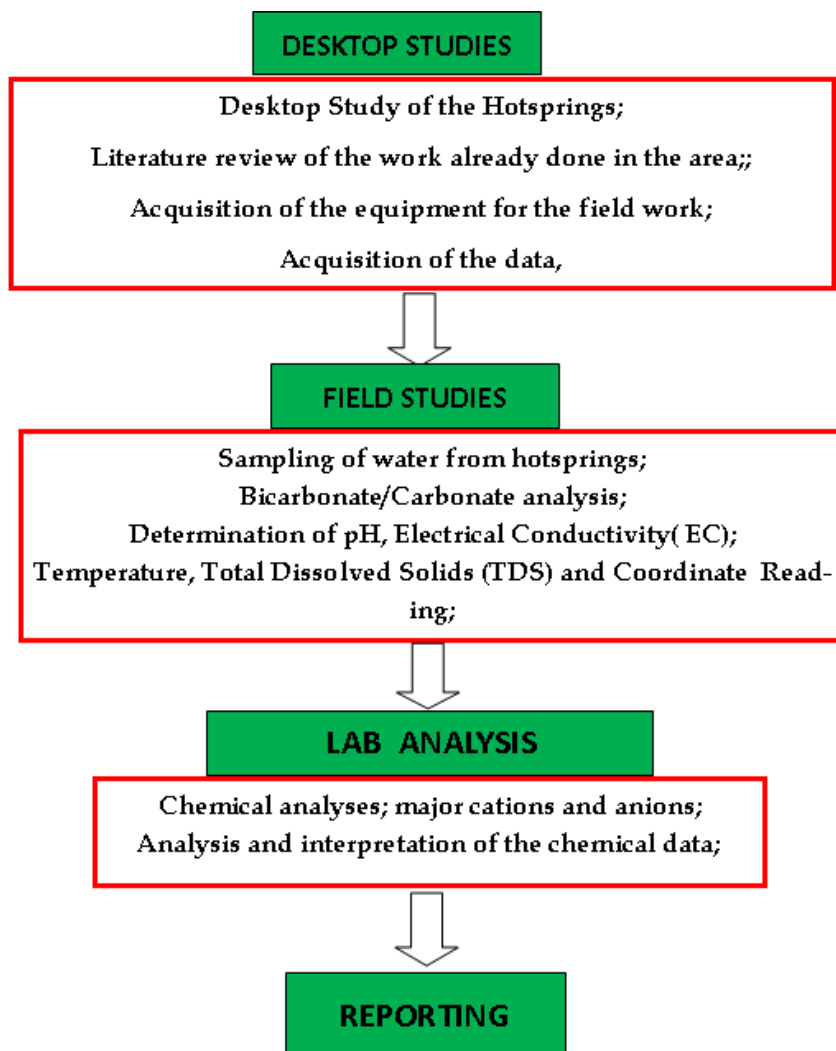


Figure 3.1: Flow chart showing the stages that were involved in the study

All field studies done were insitu determinations. Due to the variety of the aspects involved in the study, procedures followed for the different individual aspects are explained in separate

sections of this chapter. The main materials used in accomplishing this undertaking include; hot spring chemistry data, Laboratory equipments, maps, sampling bottles, Computer soft wares e.g. ArcGIS, AquaChem, Ms Office Excel, Grapher and WATCH programmes etc.

3.2. Pre-field work

The geological information for the two study areas was extracted from the studies of preceding workers (Caswell, 1953a, Cioni et al., 1992, Dunkley et al., 1994, Eshimwata and Mwinami, 2011, Griffiths, 1977, Italiana, 1987, Miller, 1952b, Tole, 1990a) who have mapped the area both from a regional point of view to a more detailed local study. Their locations were taken using GPS handset and they were plotted on the geological map of the study area (Tole, 1990a). Geological map was digitized from the available geological map of the areas using ArcGIS version 9.1.

Preliminary planning and preparation for data collection saved time and reduced the number of associated difficulties. This program took place between 29th November to 2nd December, 2011. Prior consultations were made with persons with jurisdiction over the study area notifying them of the program. The three sampling sites in Majimoto area were carefully established by making combined use of the available information from reports and maps from previous work done. The other three hot springs from Bogoria area were selected based on the ionic balance of the chemistry of the hot springs obtained from past reports (Karingithi and Wambugu, 2008).

3.3. Fieldwork

The fieldwork program was undertaken between 13th and 16th December, 2011 for the Majimoto area while chemistry data from Bogoria was derived from past geochemistry work (Karingithi and Wambugu, 2008). Samples from hot springs were taken from those with the highest measured temperature, good upflow and a good flow rate (>1 l/s). This was done to eliminate sampling hot springs that may have mixed waters (i.e. waters that are mixed with cold water). Immediate measurements of temperatures, pH, conductivity, CO₂, H₂S and total dissolved solids (TDS) were carried out on-site. Total flow rates for each discharge area were also determined using a pitot tube while temperature was determined using a thermocouple. The samples collected in 1 container which was further divided into five portions in 500ml bottles based upon the intended analysis.

The first portion was used for immediate analysis for hydrogen sulphide (H₂S), carbon dioxide (CO₂), pH, Conductivity, and total dissolved solids (TDS). To the second portion a measured amount of 5% zinc acetate solution was added to the sample for the fixation of sulphides for sulphate analysis. 1 ml of concentrated nitric acid was added to the third portion of the sample for the analysis of metal ions. The fourth portion of the sample earmarked for silica analysis was diluted ten times to avoid polymerisation of monomeric silica. The last untreated portion of the sample was reserved for the analysis of Chloride (Cl) and Fluoride (F) ions. Hydrogen sulphide gas (H₂S) were analysed at the sampling site, while carbon dioxide (CO₂), conductivity, total dissolved solids and pH were done at the end of each sampling day. CO₂ and H₂S gases in the water were analyzed using titration methods by using 0.01 M hydrochloric acid (HCl) and 0.01M mercuric acetate respectively. The bicarbonate and carbonate species concentrations were determined from the sample pH, and the titration of the sample to pH 8.3 (when the sample pH is >8.3) then to a pH of 3.8 with a standard HCl. Species concentrations were then calculated from the equilibrium reactions of carbonate and bicarbonate. Silica (SiO₂), sulphates (SO₄), Cl, F and the metals ions were analysed at the GDC main laboratory located in Nakuru. The sample collection and chemical description procedures observed was conducted in line with the sampling and analysis of geothermal fluids (Arnórsson et al., 2006). The summary of the preservation methods employed are as tabulated in Table 3.1.

Table 3.1: Preservation methods for the hotsprings and ocean water samples

Type	Method	Purpose	Used for
Physical	Filtration	Prevent interaction with suspended matter	Anions, cations
	Airtight container	Prevent interaction with atmospheric air	Volatiles
	On-site analysis	Prevent reactions of reactive constituents	Reactive constituents
Chemical	Acidification	Prevent adsorption on walls of containers	Cations
	Precipitation	Prevent a constituent from reaction to change the concentration of another	Sulphide to preserve sulphate
	Dilution	Prevent polymerization and precipitation	Silica

Field results were recorded in a field note book. These included; nature of the various hotsprings; location name of the site; sample number; date of collection; pH, TDS, and conductivity readings; and H₂S, CO₂ and bicarbonate results. Helpful information such as GPS coordinates and altitude were recorded. Water sampling from the Majimoto hotsprings and the sea water was carried out to determine its effects in the chemistry of the hotsprings.

3.4. Laboratory Methods

The choice of an analytical technique that were used depended on several factors, i.e. the availability of instruments, potential servicing facilities for different types of instruments, the presence of trained personnel, and the speed, reliability and cost of the different methods. The analysis of Calcium, Nitrate, Fluoride, Sodium and Potassium were determined using ion selective method. Ion Selective Electrode (ISE) is an electrochemical sensor, based on thin films or selective membranes as recognition elements, and an electrochemical half-cell equivalent to other half-cells of the zeroth (inert metal in a redox electrolyte). The potential difference response has, as its principal component, the Gibbs energy change associated with perm-selective mass transfer (by ion-exchange, solvent extraction or some other mechanism) across a phase boundary. The ion-selective electrode is always used in conjunction with a reference electrode (i.e. outer or external reference electrode) to form a complete electrochemical cell. The measured potential differences (ion-selective electrode vs. outer reference electrode potentials) are linearly dependent on the logarithm of the activity of a given ion in solution (McNaught and Wilkinson, 1997).

The analysis of the metals (Mg⁺ and Li⁺) was done using the Atomic Absorption Spectrophotometry method. Solutions containing magnesium are aspirated directly into an air-acetylene flame and the absorbance of the resonance line at 285.2nm is measured. Lithium is determined by aspirating the sample into an air-acetylene flame and the emission intensity at 670.8nm from lithium measured by a spectrometer (Scott and Kokot, 1975).

Chloride ions were determined by using the Argentometric titrimetric method. In the argentometric method, an indicator, potassium chromate, is added to the sample, which loosely binds up a few chloride ions. Silver nitrate solution is then titrated into the sample, producing the

fine white precipitate, silver chloride. When all the free ions are complexed in this reaction, the silver nitrate takes the bound chloride ions from the indicator, producing the blood red precipitate, silver chromate, marking the end of the titration (Korkmaz, 2001).

Sulfate ions were determined by the turbidimetric method. Determination of sulfate by this method appears to be the simplest approach for analysis of water samples. It is usually rapid and sensitive and normally does not require special skill in handling a large number of analyses at one time. Sulfate ion reacts with barium chloride in acidic solution to form a suspension of barium sulfate crystals of uniform size. The resulting turbidity is proportional to the sulfate concentration of the sample. Results are expressed as ppm (mg/L) SO_4 . Most turbidimetric methods, however, have a serious shortcoming in that they do not give reproducible results; the formation of reproducible BaSO_4 suspensions under uniform precipitating conditions is difficult.

The analysis of silica was done using the UV/VIS spectrophotometry method, whereby soluble silica reacts with molybdate ion to produce a greenish-yellow complex which is then reduced by 1-amino-2-naphthol-4-sulfonic acid to produce a blue complex which is measured at preferably 815nm or, with reduced sensitivity, at 640-700nm.

F concentrations were analyzed by the Mohr titration where fluoride concentration is measured with a specific electrode containing a lanthanum fluoride crystal and an electrometer.

3.5. Data Analysis

In order to ensure that data quality is not compromised, precision and accuracy during sampling and analysis were observed following the standardized procedures. Ionic balance was used to countercheck the accuracy and completeness of analyses. Chemistry data values whose ionic balance were below 8% were regarded as good and those that went up to 10% were regarded as fairly acceptable and interpreting them require caution. Ionic balance determination was done using Watch and AquaChem programs.

The chemical analytical data of water from the three Majimoto hot springs, the Indian Ocean and three hot springs from Lake Bogoria area have been used to evaluate the effects of sea water intrusion on the chemistry of hot springs. The analytical results from Majimoto hot springs and sea water was used to calculate the proportion of sea water in the hot springs water by using mass

balance calculations. This was done to determine the proportion of sea water in the hot spring water. The fraction of the sea water in the hot springs was used to recalculate the uncontaminated chemistry of Majimoto hot springs. The analytical results were evaluated by a series of graphic plots pioneered by (Giggenbach, 1988) to infer the origin of the fluids and their relationship with sea water relative to the potential chemical equilibrium within the geothermal systems.

A typical major cation ternary plot of chloride (Cl), sulphate (SO_4) and bicarbonate (HCO_3) was used to identify the samples that are most applicable in evaluating the potential of a liquid that has been heated by an underground heat source. According to Giggenbach (1991), Cl- SO_4 - HCO_3 ternary diagrams are used for the classification of thermal water based on the relative concentrations of the three major anions Cl- SO_4^{2-} and HCO_3^- . Chloride, which is a conservative ion in geothermal fluids, does not take part in reactions with rocks after it has dissolved. Chloride does not precipitate after it has dissolved; its concentration is independent of the mineral equilibria that control the concentrations of the rock-forming constituents. Thus, chloride is used as a tracer in geothermal investigations. The Cl- SO_4 - HCO_3 ternary diagram is one diagram for classifying natural waters (Giggenbach, 1991). Using it, several types of thermal water can be distinguished: mature waters, peripheral waters, steam-heated waters and volcanic waters. The diagram also provides an initial indication of mixing relationships. According to Giggenbach (1991), the degree of separation between data points for high chloride and bicarbonate waters may give an idea of the relative degree of interaction of the CO_2 charged fluid at lower temperature, and of the HCO_3^- concentrations which increases with time and distance travelled underground. The position in which the uncontaminated and contaminated Majimoto hot springs samples plot were evaluated relative to the position of the sea water and compared to the position of the Lake Bogoria hot springs.

The Na-K-Mg ternary was used to confirm the Cl- SO_4 - HCO_3 ternary where equilibration was evaluated. Partially equilibrated samples suggest that the fluids are mixed between the equilibrium curve with either sea water or ground water. Only the chloride-bearing springs are both in partial equilibrium with geothermal alteration mineralogy and fall in or near the mature waters field on the Cl- SO_4 - HCO_3 ternary therefore, these samples will be compared with the position of the sea water. Further, the position of the Majimoto hot springs together with the Indian Ocean waters was compared to Bogoria hot springs within the Na-K-Mg

ternary. Giggenbach (1986) suggested that this triangular diagram with Na/1000, K/100, and ζ Mg at the apices can be used to classify waters as fully equilibrated with rock at given temperatures, partially equilibrated, and immature (dissolution of the rock with or no chemical equilibrium). In the construction of the figure, Giggenbach (1988) adopted the Na/K and slightly modified K/ ζ Mg geothermometer equations given by Giggenbach and Soto (1992). The full equilibrium curve is for reservoir water compositions corrected for the loss of steam owing to decompressional boiling. Uncorrected boiled waters generally will plot slightly above the full equilibrium line. The general approach presented by Giggenbach (1988) is recommended, but with some words of caution. The temperatures and compositions at which "full equilibration" may change significantly depending on which of the many Na/K geothermometers one assumes to be correct and the mineralogy (including structural states) of the phases that are in contact with the reservoir fluid. The position of the full equilibration line also changes as the assumed K/ ζ Mg geothermometer equation changes (most uncertain at low temperatures). The uppermost Mg-poor boundary of this field corresponds to the condition in which Na/K values are controlled according to the (Giggenbach et al., 1993, Giggenbach et al., 1994) geothermometer. The lowermost Mg-rich boundary of this field corresponds to the condition in which Na/K values are controlled according to the Truesdell (1976) geothermometer.

A Cl-Li-B ternary was used to determine if the waters are coming from a common source. Lithium is used as a tracer, because it is the alkali metal least affected by secondary processes for initial deep rock dissolution, and as a reference for evaluating the possible origin of two important "conservative" constituents of geothermal waters, Cl and B. Once added, Li largely remains in the solution. The B content of thermal fluids is to some degree likely to reflect the maturity of a geothermal system; because of its volatility it is expelled during the early heating up stages. In such a case, fluids from older hydrothermal systems can be expected to be depleted in B while the inverse holds for younger hydrothermal systems. It is, however, striking that both Cl and B are added to the Li containing solutions in proportions close to those in crustal rocks. At higher temperatures, Cl occurs as HCl and B as H₃BO₃. Both are volatile and can be mobilized by high-temperature steam. They are, therefore, quite likely to have been introduced with the magmatic vapour raised above to the subsurface that leads to the formation of deep acid brine responsible for rock dissolution (Karingithi, 2000). At low temperatures the acidity of HCl increases rapidly, and is soon converted by the rock to the less volatile NaCl. B remains in

volatile form to be carried in the vapour phase even at lower temperatures. The Cl/B ratio is often used to indicate a common reservoir source for the waters. Care must, however, be taken in applying such an interpretation since waters from the same reservoir may show differences in this ratio, due to changes in lithology at depth over a field (example, the occurrence of a sedimentary horizon), or by the absorption of B into clays during lateral flow.

An expanded Giggenbach plot (Giggenbach, 1988) of magnesium/calcium (Mg/Ca) vs. potassium/sodium (K/Na) was used to illustrate progressive changes in the chemistry of the Majimoto hot springs water away from the sea water and the results compared to the position of the Lake Bogoria hot springs.

The Chloride-Enthalpy plot (Fournier and Potter, 1982) was used for interpretations of mixing scenarios between the sea water and the hot springs water. This was also related to the position of the Bogoria hot springs.

A comparative K/Mg vs. K/Ca plot (Giggenbach, 1988) was used to confirm maturity, mixture and the type of maturity taking place. The difference in maturity between the hot springs waters was related to the position of the sea water and compared to the position of the Bogoria hot springs.

A piper diagram (Piper, 1944) was plotted to show the type of water and how the sea water was influencing the chemistry of the Majimoto hot springs waters which was then compared with the Bogoria hot springs waters.

Chapter 4

4. Results

4.1. Chemical Analytical Results

A total of 7 water samples were analyzed for chemistry in the two study areas. These comprised of 3 hot springs from Majimoto, 3 hot springs from Bogoria and one sample from the Indian Ocean waters. The hot springs are characterized by mild altered grounds. Temperatures of up to 63°C were measured from the hot springs at Majimoto 3, 66°C at Majimoto 2 (with high H₂S gas smell and CO₂ gas emission) and 57.5°C at Majimoto 1. The resultant chemical compositions of the samples have been presented in Table 4.1.

Table 4.1: Analytical Chemistry results

Sample	Temp °C	pH @20°C	Cond µs/cm	TDS ppm	HCO ₃ ppm	H ₂ S ppm	Cl ppm	SO ₄ ppm	SiO ₂ ppm	B ppm	Na ppm	K ppm	Mg ppm	Ca ppm	Li ppm
Majimoto 3	57.6	7.2	10160	5090	700	0.03	2503	1.6	46	2.7	2170	50.9	33.4	8.1	0.01
Majimoto 2	66.1	7.6	8130	4070	712	0.52	1860	2	54	1.9	1428	50.6	13.6	12.8	1.9
Majimoto 1	63.3	7.5	8590	4300	671	0.03	2045	1	56	2.6	1397	45.9	16.4	1.4	1.9
Bogoria hot spring 1	89	9.2	5122	2560	2057	0.51	602	14.7	126	0.3	142	36.9	0	1.3	0.3
Bogoria hot spring 2	86	8.8	4880	2440	2240	0.17	544	11.6	77	0.9	124	36.7	0	7.8	0.3
Bogoria hot spring 3	96	9.3	5627	2810	2206	0.43	669	10.9	185	0.7	14.2	4	0	3	0.3
SEAWATER	20	8	-	313,600	142	-	18,980	2649	10	5	10,561	380	1272	400	-

The chemical composition of the Majimoto hot springs water is presented in Table 4.1 above. The pH of the Majimoto waters scatters around the neutral value with a range of 7.2 to 7.6. Total carbonates concentrations showed a range between 671 ppm and 700 ppm. Chloride is the dominant anion with readings of over 1800 ppm for the Majimoto hot springs. H₂S concentrations were observed to very low probably due to oxidation. Anomalous values are observed for calcium and magnesium especially in the Majimoto waters where low values are expected due to their brackish characteristics. The Majimoto waters are highly mineralized but not to the levels of Magadi and Homa Bay, other prospects in Kenya, which record TDS values of over 45,000 ppm and over 30,000 ppm respectively (Armannsson, 1987, Jones et al., 1977, Tole, 1996). Calcium and magnesium both have high concentrations and are among the highest recorded in all the Kenyan geothermal systems. Magnesium concentration range from 14 ppm to 138 ppm whereas calcium concentration lies in the range of 1.4 ppm to 129 ppm. This suggests an intrusion of the sea water into the waters of the hot spring.

The chemical compositions of analysis of the Bogoria hot spring water are also as tabulated in Table 4.1. The temperature of the water discharged by the hot springs varied between 86°C and 96°C. The pH varied from 8.8 to 9.3 with conductivity ranging between 345-385µS/cm. The Bogoria waters are characterised by high bicarbonate ranging 2057-2240ppm. High bicarbonates discharged by the Bogoria waters are due to the influence of the Rift Valley where CO₂ flux is high contributing to high concentrations of bicarbonates (Karingithi and Wambugu, 2008).

4.2. Proportion of Sea Water in the Geothermal Water

To understand the influence of the sea water in the geothermal water in the Majimoto springs and to recalculate the concentrations of the uninfluenced water, it is important to calculate the proportion of the sea water in the Majimoto waters. The calculation of the proportion of the sea water was achieved by mass balance of individual chemical constituents of the spring waters with the sea water.

4.2.1 Mass Balance

To calculate the proportion of the sea water in the Majimoto springs water, magnesium cation was used. Magnesium cation concentration in geothermal fluid is usually found in very minute concentrations, almost zero concentration. For this reason, magnesium cation was used since it is the only constituent which we can assume to be zero in geothermal fluid. Using this assumption, we can create a mass balance equation as follows;

$$Mg_{spring} = Mg_{geothermal} (1 - X) + Mg_{seawater} X \quad \text{Equation 1}$$

Where;

Mg_{spring} = Magnesium concentration in hot spring water

$Mg_{geothermal}$ = Magnesium concentration in geothermal water

$Mg_{sea\ water}$ = Magnesium concentration in sea water

X = Proportion of sea water

Further;

$$Mg_{spring} = Mg_{geothermal} - Mg_{geothermal} X + Mg_{seawater} X \quad \text{Equation 2}$$

$$Mg_{spring} = Mg_{geothermal} - Mg_{geothermal}X + Mg_{seawater}X \quad \text{Equation 3}$$

Therefore;

$$X = \frac{Mg_{spring} - Mg_{geothermal}}{Mg_{seawater} - Mg_{geothermal}} \quad \text{Equation 4}$$

If we assume that the concentration of magnesium in geothermal water is zero, then Equation 4 becomes;

$$X = \frac{Mg_{spring}}{Mg_{seawater}} \quad \text{Equation 5}$$

If we use the sea water and Majimoto 3 chemistry results to calculate the proportion of sea water in the spring water using the above equation;

$$X = \frac{33.4}{1272}$$

$$X = 0.03$$

The above calculation denotes that 3% of sea water chemistry is found in the Majimoto 3 spring. If we use the same calculation for the Majimoto 2 and Majimoto 1 hot springs then 1% and 1.3% respectively of sea water is found in the mentioned waters.

4.2.2 Geothermal Water Chemistry

The value of X was further used to recalculate the concentrations of individual chemical constituents of the Majimoto springs without the sea water influence in the water to understand the chemistry of the water without the sea water.

$$Cl_{spring} = (1 - X)Cl_{geothermal} + XCl_{seawater} \quad \text{Equation 6}$$

$$= Cl_{geothermal} - XCl_{geothermal} + XCl_{seawater} \quad \text{Equation 7}$$

$$= Cl_{geothermal} + X(Cl_{seawater} - Cl_{geothermal}) \quad \text{Equation 8}$$

Therefore;

$$Cl_{geothermal} = \frac{Cl_{spring} - XCl_{seawater}}{(1 - X)} \quad \text{Equation 9}$$

$$= \frac{2,503 - 0.03(18,980)}{(1 - 0.03)}$$

$$= 1916 \text{ ppm}$$

The results indicate that chloride concentration of the recalculated geothermal water is lower than the sampled concentration due to the influence of sea water. Similar calculations were undertaken for bicarbonate, sulphate, boron, sodium, potassium, magnesium, calcium and lithium (Table 4.2).

Table 4.2: Recalculated Majimoto springs water without sea water influence

Sample	Temp °C	pH @20°C	Cond µs/cm	TDS ppm	HCO3 ppm	H2S ppm	Cl ppm	SO4 ppm	SiO2 ppm	B ppm	Na ppm	K ppm	Mg ppm	Ca ppm	Li ppm
Majimoto 3a	57.6	7.2	10160	5090	695.6	0.01	1916	0.01	45.69	2.545	1843	39.15	0.01	0	0.01
Majimoto 2a	66.1	7.6	8130	4070	707.6	0.01	1273	0.01	53.69	1.745	1101	38.85	0.01	0.4	1.9
Majimoto 1a	63.3	7.5	8590	4300	666.6	0.01	1458	0.01	55.69	2.445	1070	34.15	0.01	0	1.9

Comparative analyses (Table 4.1 and 4.2) illustrate that the chloride-rich springs of Majimoto are to a small degree re-worked seawater. This is because, the extremely high Mg in the chloride-rich hot springs requires an origin from either evaporites or seawater and there is no evidence of evaporite deposits on Majimoto. The high chloride content of the fluids does not by itself require seawater but the chloride content is closely linked to high magnesium and the magnesium content of seawater is very high. The recalculated Majimoto waters indicate very low concentrations of H₂S, SO₄ and Mg.

4.3. Type of Hotspring Water

The type of water discharging from the hot springs was evaluated by using the Cl-SO₄-HCO₃ and CL-Li-B ternary diagrams.

4.3.1 Cl-SO₄-HCO₃ Ternary Diagram

The type of hot springs water was evaluated using Cl-SO₄-HCO₃ ternary diagram. The analytical results were evaluated by a graphical plot pioneered by (Giggenbach, 1991, Giggenbach, 1988) to infer the origin of the fluids relative to the potential chemical equilibrium in an active geothermal reservoir. A standard major anion ternary plot (Figure 4.1) after Giggenbach (1991) of chloride (Cl) sulfate (SO₄) and bicarbonate (HCO₃) identifies the samples that are most relevant in evaluating the potential of a liquid dominated geothermal prospect.

According to the results of the diagram (Figure 4.1), both the original and the recalculated Majimoto spring water plot at the mature region. On the other hand, the Bogoria waters plot at the peripheral region implying that they are discharging waters with high bicarbonate at the margins of the field. This high bicarbonate is also associated with the high CO₂ flux that is experienced along the Rift Valley. The Bogoria hot springs also show low concentrations of Cl and B indicating limited residence time and limited water rock interactions in the reservoir supplying these hot springs. Bi-carbonate waters mainly form due to mixing of high Cl waters with near surface ground waters and also due to condensation of CO₂ in near surface waters (Karingithi and Wambugu, 2008).

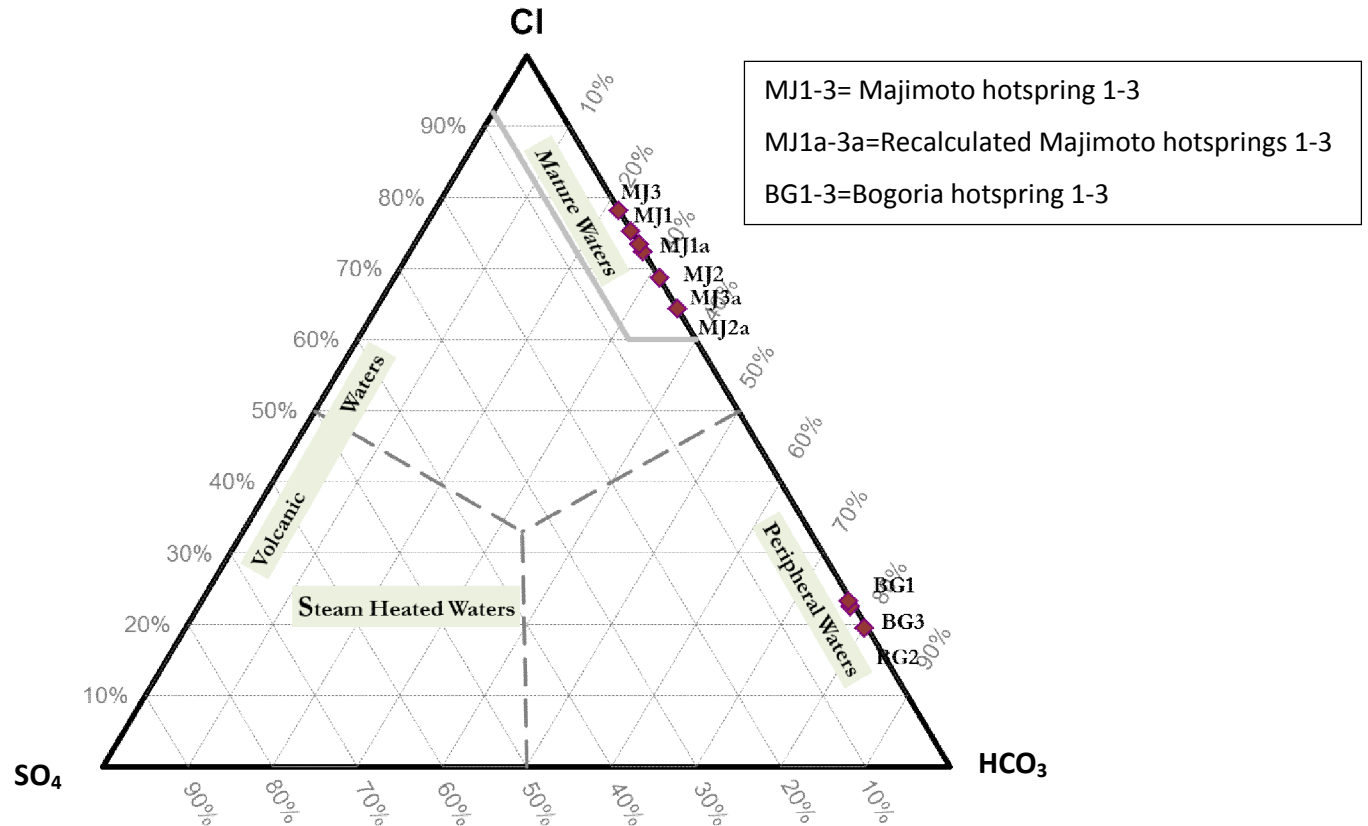


Figure 4.1: Relative Cl-SO₄-HCO₃ ternary diagram showing the origin of fluids relative to chemical equilibrium in the reservoir

Although the hot springs are discharging water at the local boiling point and contain high amounts of dissolved CO₂. It is possible that these springs result from ground waters being heated by steam and due to the high CO₂ levels, the bi-carbonate content increases in the waters. Most of the hot springs within the Rift Valley contain high bicarbonate concentrations hence most will plot at the high bicarbonate region within the ternary diagram.

As far as the Majimoto hot springs waters are concerned, they plot at the Cl-HCO₃ axis at the mature region. They are therefore considered to be originating from deep geothermal reservoirs as proposed by Giggenbach (1988). It is also clear from the diagram that the sea water has had a small influence on the maturity of these waters.

4.3.2 Cl-Li-B Ternary Diagram

To determine if the hot spring waters are from a common source the relative Cl, Li and B ternary has been used (Figure 4.3). The potential origin of the hot spring waters as seawater is also

consistent with the close affiliation of the Majimoto hot spring waters with seawater in a ternary plot of chloride (Cl) lithium (Li) and boron (B). The original Majimoto springs water are seen to plot very close to the apex of the ternary and close to the sea water. This may also indicate that they are from old hydrothermal systems and that the fluid migrates from the old basement rock. However the Bogoria and the recalculated Majimoto spring waters plot beneath emphasizing the influence of the sea water to these springs.

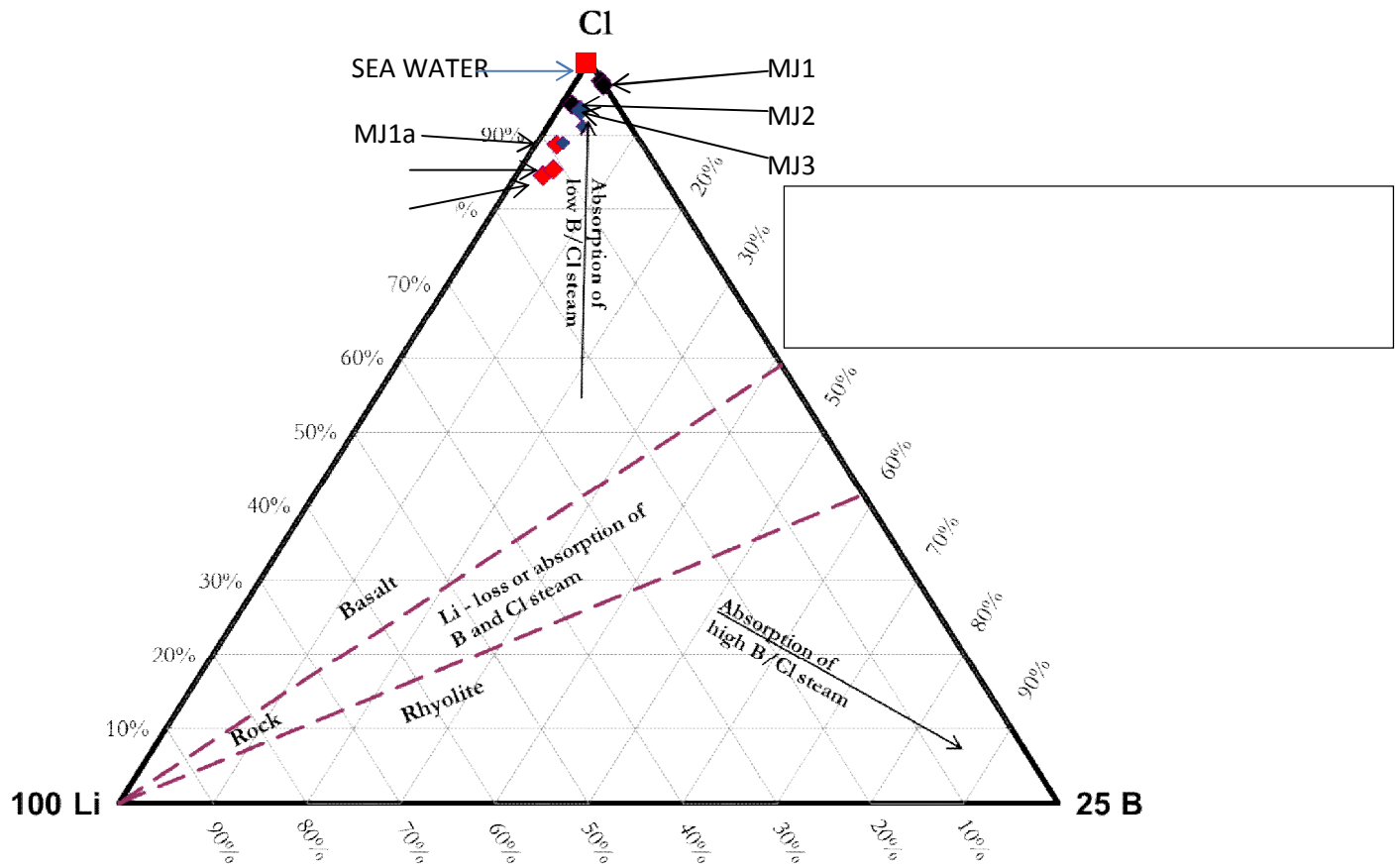


Figure 4.2: Cl-Li-B Ternary Diagram showing the different sources of the waters relative the sea water

4.4. Progressive Changes in the Chemistry of the Hotsprings Away from Sea Water

The progressive change in the chemistry of the hotsprings water away from the sea water was evaluated using the Na-k-Mg-Ca diagram.

4.4.1 Na-K-Mg-Ca Diagram

To illustrate the progressive changes in chemistry of the Majimoto waters away from the sea water the Na-K-Mg-Ca diagram was used (Figure 4.4). By the comparison with the compositions of waters produced through isochemical dissolution of crustal rocks such as basalts (BA), granite (GR) and the average crust (AC) (Taylor, 1964) and the composition of waters expected for equilibrium with an isochemically recrystallized, thermodynamically stable average crustal rock (Giggenbach, 1986), only the deep well discharges appear to achieve full water-rock equilibrium. The acid waters and the soda springs occupy positions suggesting varying degrees of approach to full equilibrium at lower temperatures. Most neutral chloride waters appear to follow a common curved trend suggesting the transition from rock dissolution to rock equilibration to be a process more complex than a simple end member mixing.

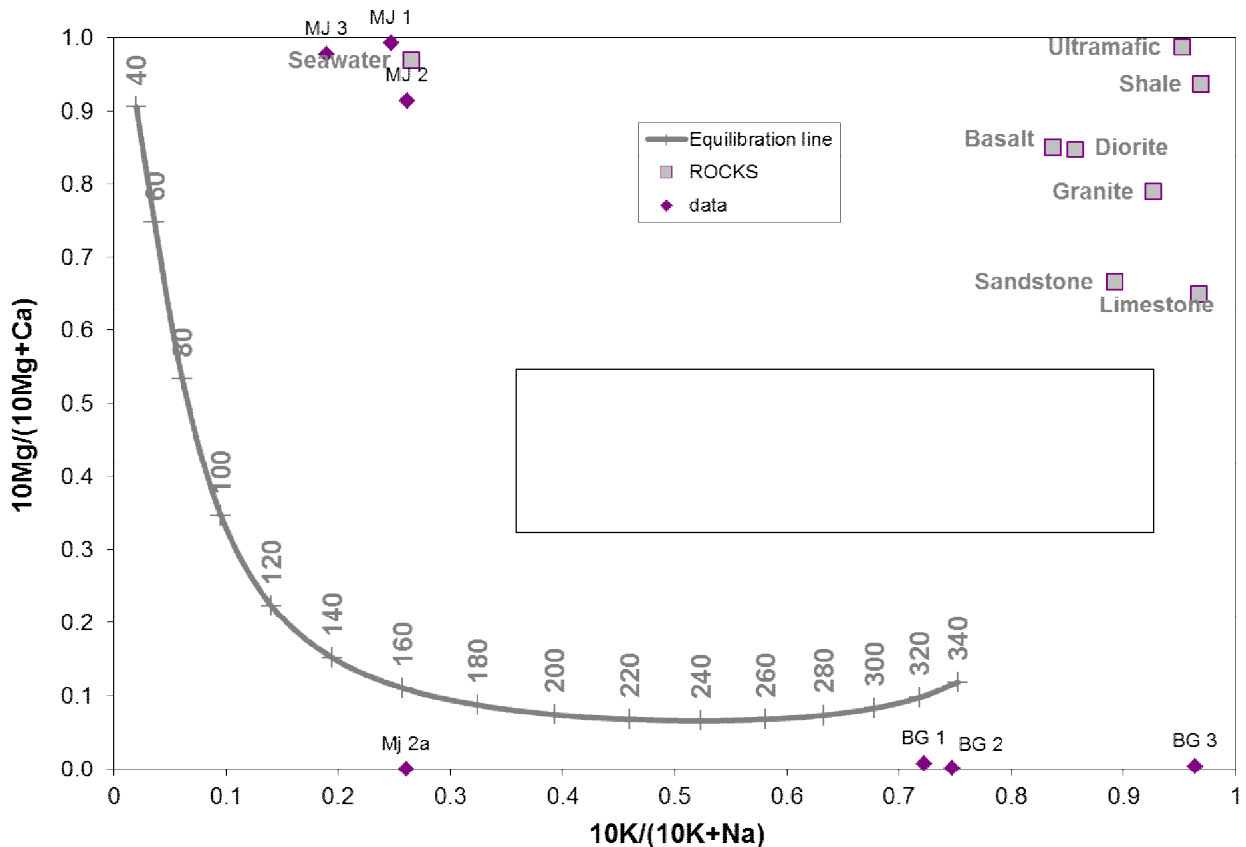


Figure 4.3: Na-K-Mg-Ca Diagram showing the changes in chemistry of the Majimoto and Bogoria water away from the sea water

A more detailed evaluation of this rock-dissolution, rock equilibration processes requires the set of four cations to be subdivided into several sub-sets such as Na-K, K-Mg, and K-Ca. According to the diagram, it is quite clear that the original Majimoto waters plot close to the sea water indicating the close relationship that exists between these two types of waters. Majimoto 2 hot spring plotted slightly below the sea water but on the same line as the sea water indicating that it is least affected by the sea water as compared to the rest of the hot springs. The Mg/Ca ratio for the Majimoto waters suggests that the liquid is still depleted in Mg relative to limestone (a possible surrogate of evaporite deposits). The K/Na ratio suggests that the liquid was exposed to higher temperatures, up to 160°C shown by a vertical projection to the equilibrium line. All the samples of the recalculated Majimoto springs plotted at the same point represented by MJ2a. These samples plotted below the equilibrium line and directly below the original Majimoto hot spring waters. This indicates that the sea water influence is of significant effect to this chemistry whereby it is seen that uncontaminated spring water is progressively changed from unequilibrated state to equilibrated state with characteristics of sea water.

In the case of the Bogoria waters which are far from the sea water, there is no relationship that exists between these waters and the sea water. They are plotting on the unequilibrated region with very low magnesium concentrations.

4.5. Maturity, Equilibration and Geothermometry

Maturity, equilibration and geothermometry of the hot spring water were evaluated using the Na-K-Mg ternary diagram and the geothermometry calculations.

4.5.1 Na-K-Mg Ternary Diagram

The influence of sea water on maturity and equilibration was evaluated using the Na-K-Mg triangular diagram. The diagram was also used to emphasize the conclusion that the mature samples from the Cl-SO₄-HCO₃ ternary are the most reasonable samples in considering the geothermal potential. A Giggenbach Na-K-Mg ternary plot (Figure 4.2) shows these same samples are near the partial equilibrium portion of the diagram suggesting that the Majimoto waters are mixed fluids that occur between the equilibrium curve and either seawater or shallow groundwater (Mg-apex).

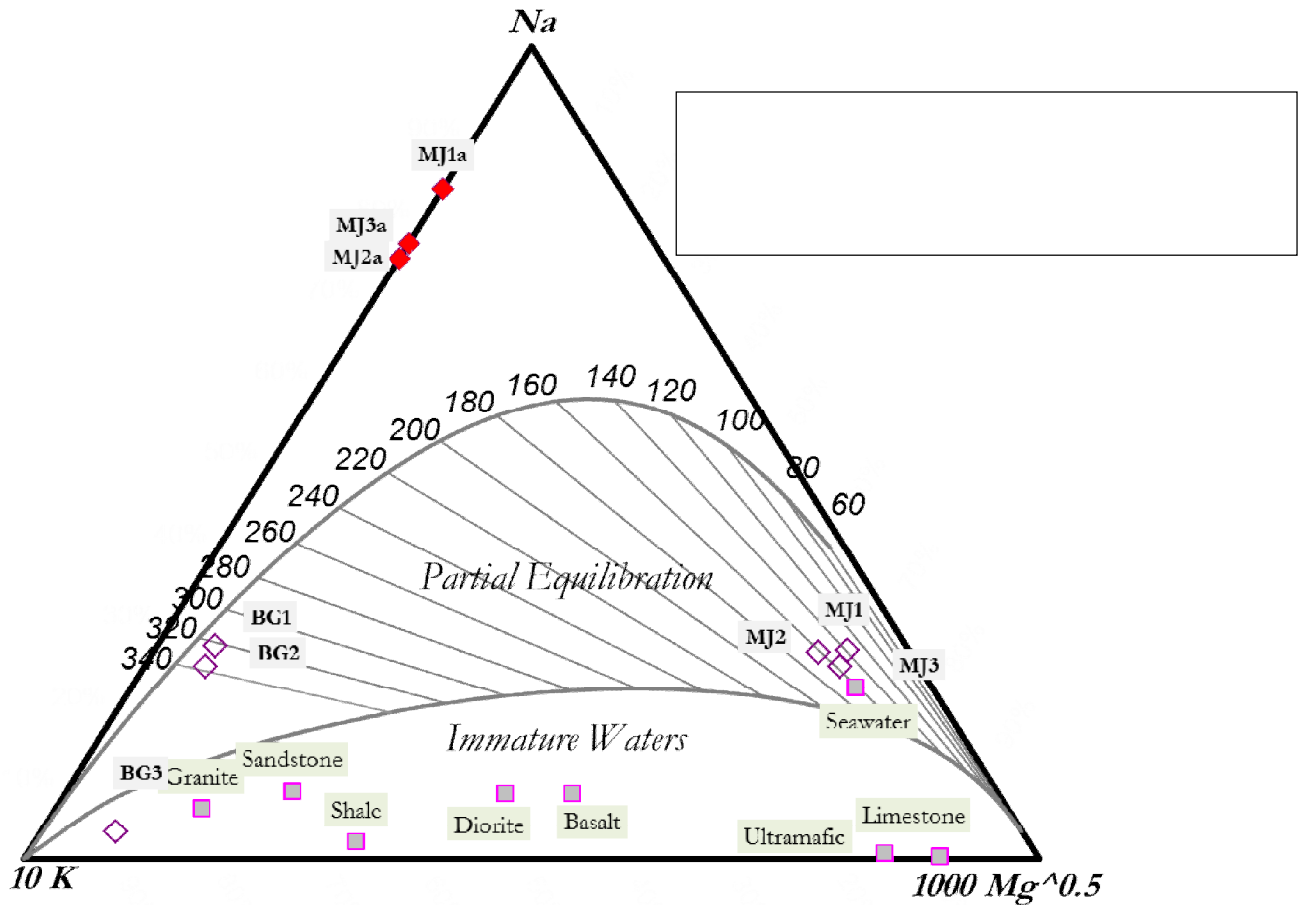


Figure 4.4: Na-K-Mg Ternary Diagram showing how the sea water has influenced the original Majimoto hot spring waters

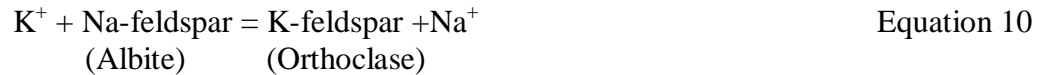
According to the results of the diagram, the original Majimoto waters plotted at the partially equilibrated region close to the sea water indicating that a close relationship exist between these two waters. While the recalculated Majimoto waters plotted above the equilibration line. A small dilution is necessary to explain the difference between seawater and the original Majimoto waters. In ideal situations only the chloride-bearing springs are both in partial equilibrium with geothermal alteration mineralogy (Figure 4.2) and fall in the mature waters field on the Cl-SO₄-HCO₃ ternary plot (Figure 4.1) therefore, only the original Majimoto chemistry compares with sea water. The original Majimoto chemistry (MJ1a, MJ2a and MJ3a), however, cannot give reliable geothermometry temperatures due to the influence of the sea water. Its also evident that the chemistry of the sea water has significant effect on the degree of equilibration of geothermal waters. As seen in the diagram, the sea water has influenced the maturity of the Majimoto

springs. The original Majimoto spring water plot at the partially equilibrated region while the recalculated Majimoto spring water without the sea water plot above the full equilibrated line. These results also give an initial indication that the sea water has an influence on the geothermometry temperatures.

In the case of the Bogoria waters (BG1 and BG2), they plotted close to the fully equilibrated region indicating that the fluids are closely equilibrated with respect to sodium and potassium minerals. As such, the use of Na-K geothermometer is justified. Its clear that these waters are pure geothermal waters and they have partially interacted with the host rocks. Its quite clear from these results that sea water has influenced the equilibration of the Majimoto waters.

4.5.2 Geothermometry

Two geothermometry functions were tested using the chemistry of the original and recalculated Majimoto springs. The Na-K and K-Mg geothermometers were applied. The Na-K geothermometer was selected because it is based on ion exchange reactions whose equilibrium constants are temperatures dependent involving partitioning of Na and K between hydrothermal altered aluminum silicates and solutions. The ratio is related to the general exchange reaction (Equation 10);



The equilibrium constant, K_{eq} , for Equation 10 is;

$$K_{eq} = \frac{[\text{KAlSi}_3\text{O}_8][\text{Na}^+]}{[\text{NaAlSi}_3\text{O}_8][\text{K}^+]} \qquad \text{Equation 11}$$

And if the activities of the solid reactants are assumed to be in unity and the activity of the dissolved species is about equal to their molal concentrations, then Equation 11 will be reduced to:

$$K_{eq} = \frac{[\text{Na}^+]}{[\text{K}^+]} \qquad \text{Equation 12}$$

The following formulae, based on empirical correlation, presented by Arnorsson et al. (1983) and Giggenbach (1988), are used in this report; the concentrations of Na and K are in mg/kg:

Na/K temperature by Arnorsson et al. (1983) is as given in Equation 13;

$$t \text{ } ^\circ\text{C} = \frac{933}{0.993 + \log(\text{Na/K})} - 273.15 \quad \text{Equation 13}$$

Na/K temperature by Giggenbach (1988)

$$t \text{ } ^\circ\text{C} = \frac{1390}{1.75 + \log(\text{Na/K})} - 273.15 \quad \text{Equation 14}$$

The K-Mg geothermometer is based on the equilibrium between water and the mineral assemblage K-feldspar, K-mica and chlorite (Giggenbach, 1988). It is found that it responds fast to changes in the physical environment and, thus, usually gives a relatively low temperature in mixed and cooled waters as compared to other geothermometers (concentrations are in mg/kg) (Equation 15):

$$t \text{ } ^\circ\text{C} = \frac{4410}{14.0 - \log(\text{K}^2/\text{Mg})} - 273.15 \quad \text{Equation 15}$$

The results for the geothermometry temperatures are as tabulated in Table 4.3. According to the results there is a temperature difference of 5°C for Majimoto 1 spring between the original and recalculated springs for the Na/K geothermometer. However, as for the K/Mg geothermometer no results were obtained since the recalculated Majimoto chemistry had very low magnesium concentrations. As for the case of the Bogoria springs they gave high temperatures due their location and unmixed nature.

Table 4.3: Calculated geothermometry temperatures

Sample Name	Na/K (°C) (Giggenbach)	K/Mg (°C) (Giggenbach)
Majimoto 1	138	93
Majimoto 2	161	105
Majimoto 3	157	99
Majimoto 1a	133	-

Majimoto 2a	158	-
Majimoto 3a	154	-
Bogoria Spring 1	322	291
Bogoria Spring 2	337	291
Bogoria Spring 3	-	293

4.6. Mixing Scenarios

The different mixing scenarios were evaluated using a Chloride-Quartz Geothermometer Enthalpy diagram, comparative K/Mg vs. K/Ca cross plot and piper diagram.

4.6.1 Chloride-Quartz Geothermometer Enthalpy Diagram

A Chloride-Quartz Geothermometer Enthalpy diagram was used in the interpretation of mixing scenarios (Maturgo et al., 2000). In this diagram chloride is the main anion in alkali chloride waters (Ellis and Mahon, 1977). Chloride concentration is not related in a simple way to the subsurface temperatures in springs with high chloride content and its use as a geothermometer is not common. Truesdell and Fournier (1976) have suggested a method to calculate the subsurface temperature from chloride content and enthalpies of the fluids from the thermal, cold and mixed springs. The range of chloride concentrations can give information about the minimum temperature of the reservoir that feeds the springs. When this range appears to result mainly from different extents of boiling such data is used to estimate the temperature of the reservoir.

Enthalpy-chloride diagrams have been used to predict underground temperatures, salinity, boiling and mixing relationships. Fournier (1977) suggested the use of an enthalpy-chloride diagram to predict underground temperature. This mixing model takes into account both mixing and boiling processes. Its application basically involves relating analyzed chloride levels to water enthalpy, which can be derived from measured discharge temperature, geothermometry temperature and silica-enthalpy mixing model temperature.

According to the Chloride-Quartz Geothermometer Enthalpy diagram (Figure 4.5), there is no relationship between the Bogoria and Majimoto hot springs. The two waters have distinctly different trends of mixing. High chloride Majimoto waters appear to lie on different mixing lines with the Bogoria waters. The original Majimoto hot springs water and the recalculated Majimoto springs water indicate a close relationship. It appears that the original Majimoto are being diluted

to form the recalculated Majimoto springs. This indicates that the sea water is the main cause of the elevated chloride levels.

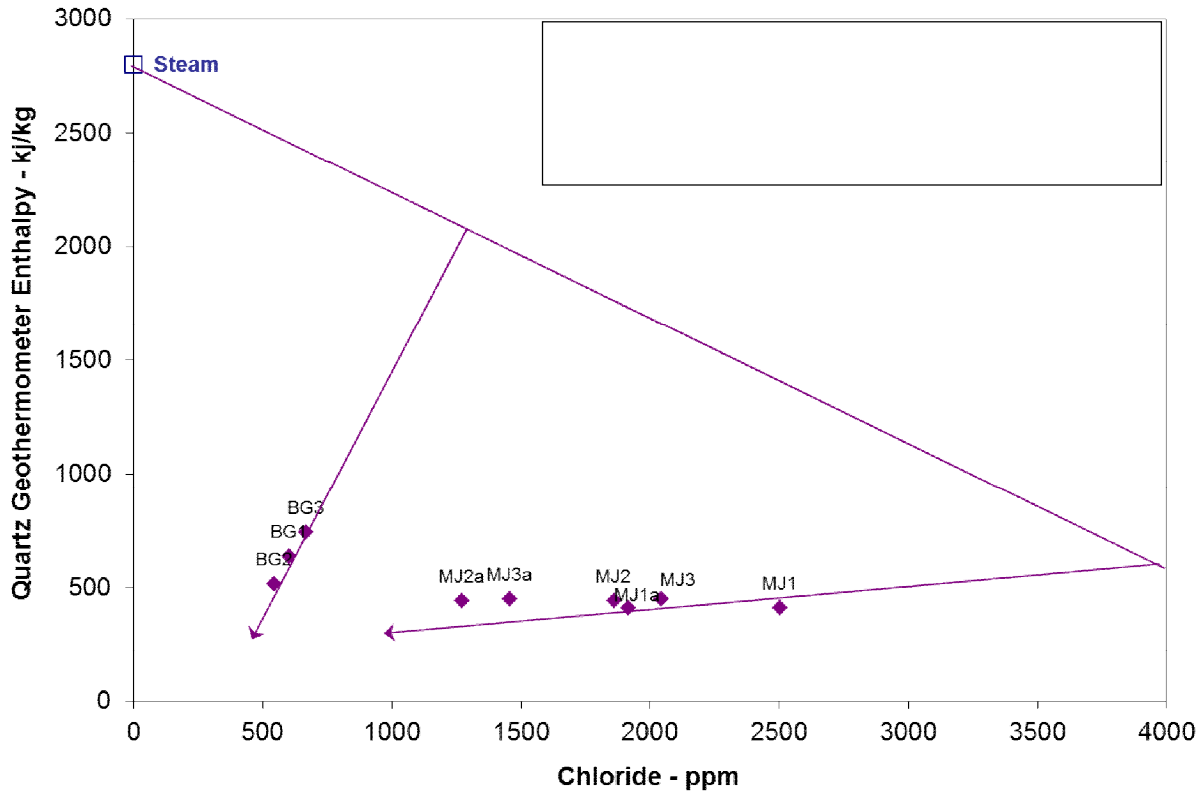


Figure 4.5: Chloride-Quartz Geothermometer Enthalpy diagram showing the different trends of mixing between the Majimoto and Bogoria waters

4.6.2 Comparative K/Mg vs. K/Ca plot

Giggenbach and Goguel (1989) refer to the comparative K/Mg vs. K/Ca cross plot as a geothermometer rather than a geothermometer plot because it juxtaposes the potassium-magnesium geothermometer with a measure of the partial pressure of CO_2 based upon equilibrium between K-feldspar, calcite and K-mica on one side and dissolved Ca^{+2} and K^+ on the other. The purpose of the cross-plot is to determine the partial pressure of CO_2 at the last temperature of the water equilibration with rock, as determined by the K-Mg geothermometer. Given that, values of the CO_2 partial pressure (P_{CO_2}) assume equilibrium between calcite and the other mineral phases, P_{CO_2} of analyses plotting outside the calcite formation field can only be interpreted qualitatively. The results of the comparative K/Mg vs. K/Ca plot (Figure 4.6) confirms that the Majimoto hot springs waters are slightly immature and are either mixed or part

of a flow-through type convective system. The position of the sea water is far from full equilibrium line close to the ultramafic dissolution line suggesting that the sea water represents a solute system far from any equilibrium involving minerals likely to control fluid chemistry in the geothermal systems. All Majimoto waters plot below the equilibrium line and close to the sea water showing the close association they have with the sea water. While the entire Bogoria waters plot above the equilibrium line.

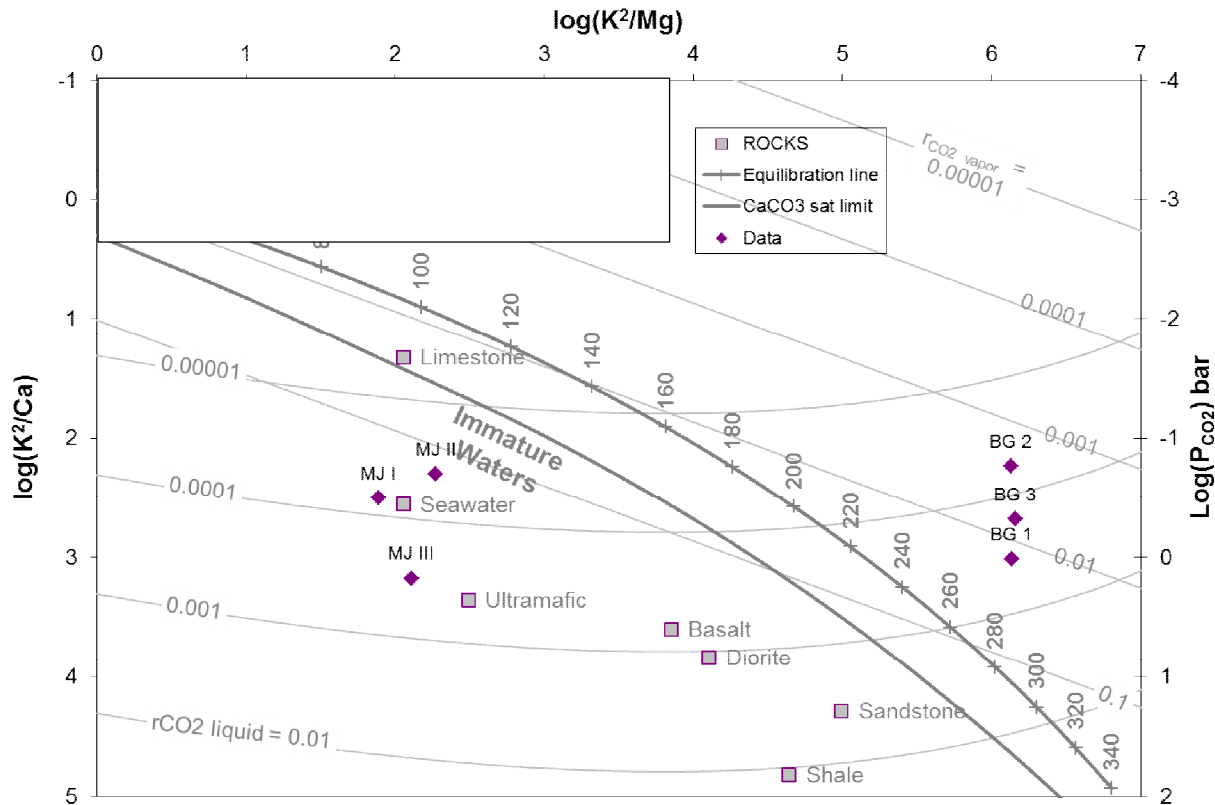


Figure 4.6: K/Mg vs. K/Ca plot showing the position of the Majimoto waters in respect to the equilibrium line.

4.6.3 Piper Diagram

Evaluation of the type of water and their relationship was achieved by the piper diagram. The piper diagram is a bi-dimensional plotted diagram composed by three different sections, two triangles and a diamond-shaped one (Figure 4.7). The use of piper diagrams is well suited when one wants to graphically represent the components of a sample of water in terms of the ions

(cations and anions) contained. The two triangular sections represent, respectively, the concentrations of the cations and anions in the water sample, while in the diamond-shaped region the information contained in the two triangles are summarized.

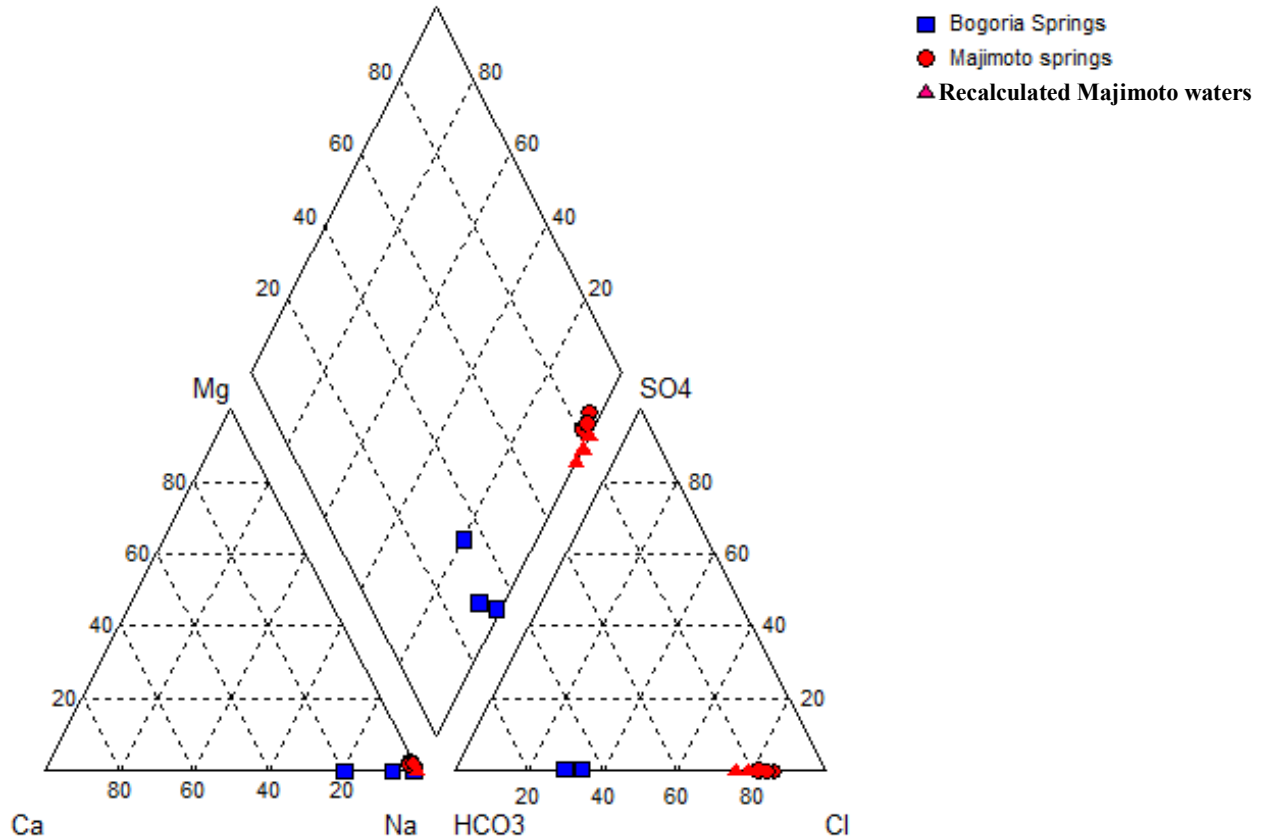


Figure 4.7: Piper diagram showing the different types of waters

The results indicate that the two Majimoto waters are purely Na-Cl type of water. Sea water is also typical Na-Cl type of water. This could only suggest that sea water is a component of the chemistry of the Majimoto springs. These waters commonly occur as the discharge from hot springs in low temperature systems, and are mostly restricted to the margins of major outflow structures and upflow zones in high temperature systems. As for the case of the Bogoria hot springs, they are purely Na-HCO₃ type of water. These waters are typical carbonate water which are products of gas and steam condensation (CO₂ and H₂S) into poorly oxygenated sub-surface groundwater. CO₂-rich fluids and neutral bicarbonate-sulphate water are included within the bicarbonate group. Bicarbonate waters are typically found on the margins of volcanic

geothermal areas and can occur in umbrella shaped perched aquifers overlying the geothermal system.

Chapter 5

5. Discussion

Sea water intrusion in coastal aquifers is usually a common contamination problem that occurs in the coastal areas (El-Bihery and Lachmar, 1994). Water formed by mixing geothermal water with sea water and cold groundwater or surface water may possess chemical characteristics which serve to distinguish it from unmixed geothermal water (Henry, 1959, Xue et al., 1993, Todd and Mays, 1980). The reason is that the chemistry of geothermal water is characterized by equilibrium conditions between solutes and alteration minerals, whereas the composition of cold water appears mostly to be determined by the kinetics of the leaching process. The residence time in the bedrock after mixing and the temperature and salinity of the mixed water have an influence on the final chemical composition in the spring discharge. Geothermal waters are often, but not always, much higher in dissolved solids than cold ground and surface waters but much less dissolved in solids than the sea water (Henry, 1959, Xue et al., 1993, Todd and Mays, 1980). Most of the hot springs throughout the rift valley do not show chemical characteristics of the dissolved solids as the Majimoto waters (Macdonald et al., 1987, McCall, 2010, Renaut et al., 1998, Tarits et al., 2006, Cioni et al., 1992, Leat et al., 1984). Strong conductive cooling of geothermal waters in up flow zones and subsequent reactions with the rock may produce compositional affinities similar to those obtained by leaching subsequent to mixing. The main chemical characteristics of sea mixed water, which serve to distinguish them from equilibrated typical geothermal waters, include very high concentrations of silica in relation to the discharge temperature, low pH relative to the water salinity and high total carbonate, at least if the mixing has prevented boiling and the temperature of the hot water component exceeds some 200°C (Henry, 1959, Todd and Mays, 1980, Xue et al., 1993). Sea water tend to be calcite undersaturated and with low calcium/proton activity ratios compared with geothermal waters (Arnórsson, 1985). Very few studies have been done that touch on the influence of sea water on the chemistry of hot springs all over the world. This is because generally, coastal areas comprise

of low lands with small gradients bordering estuaries/sea and or lower reaches of rivers, coastal marshes, lagoons and in rare cases hot springs.

This chapter discusses the results obtained from the chemical analysis of water from hot springs from Majimoto hot springs, Bogoria and Indian Ocean waters. This would include interpretations of the chemical data using mass balance, Na-K-Mg ternary, Cl-SO₄-HCO₃ ternary, Relative Cl, Li and B ternary, Na-K-Mg-Ca diagram, Chloride-Quartz Geothermometer Enthalpy diagram, Comparative K/Mg vs. K/Ca geothermometer plot, Piper diagram and Chloride Variation diagrams.

The main objective of this study was use thermal fluids from Majimoto and Bogoria and the sea water to evaluate the effects of sea water on the chemistry of hot springs. Specific objectives of this study include calculating the proportion of sea water in the hot springs water, assessing the type of hot springs waters and how the sea water has influenced this chemistry, ascertaining the influence of sea water on the maturity and equilibration of the hot springs waters and investigating the progressive changes in the chemistry of the hot springs away from the chemistry of the sea water.

In the quest of finding out the proportion of sea water on the chemistry of hot springs, mass balance equations were used to achieve this. In the mass balance equation, magnesium cation was used since it is the only constituent which we can assume to be zero in geothermal fluid. The results indicate that 3% of sea water is found in the Majimoto spring confirming the presence of mixing.

While assessing the type of hot spring water and how the sea water has influenced its chemistry, the Cl-SO₄-HCO₃ ternary diagram was used. The Cl-SO₄-HCO₃ ternary diagram indicates that the sea water did not affect maturity of hot springs waters. This is because both the original and the recalculated Majimoto spring water plot at the mature region. However, the recalculated Majimoto spring chemistry water is seen to possess more bicarbonate compared to the original Majimoto. The Cl-Li-B ternary diagram was also used to support this conclusion whose results indicates a close relationship between the original majimoto hot springs water and the sea water. This proposes the potential origin of the hot spring waters as seawater. The original Majimoto springs water are seen to plot very close to the apex of the ternary and close to the sea water; this

may indicate that they are from old hydrothermal systems and that the fluid migrates from the old basement rock.

While seeking to investigate the progressive changes in the chemistry of the hot springs away from the chemistry of the sea water the Na-K-Mg-Ca diagram was used. The Na-K-Mg-Ca diagram results indicate that the original hot springs water have a progressive change in chemistry towards the sea water as opposed to the recalculated chemistry which indicates a progressive change in chemistry away from the sea water. The recalculated hot springs waters plot below the equilibrium line while the original hot springs water plot above the equilibration line and close to the sea water reflecting the close relationship that exists between these two waters.

In ascertaining the influence of sea water on the maturity, geothermometry and equilibration of the hot springs waters, the Na-K-Mg ternary was used. The results of the Na-K-Mg ternary confirm that sea water indeed affects the degree of hot springs water, whereby, contaminated hot springs water is partially equilibrated compared to uncontaminated hot springs water which is equilibrated. These results show that the original Majimoto waters plotted at the partially equilibrated region close to the sea water indicating that a close relationship exists between these two waters, while the recalculated Majimoto waters plotted above the equilibration line. A small dilution was however, necessary to explain the difference between seawater and the original Majimoto waters. The geothermometry results designate geothermometry temperatures of Majimoto hot springs to be 138°C, while the recalculated Majimoto springs give a geothermometry temperature of 133°C according to the Na/K geothermometer. This indicates a lowering of temperature of up to 5°C suggesting that sea water actually lowers the geothermometry temperatures of hot springs and indeed giving erroneous interpretations.

While also seeking to investigate and illustrate the mixing scenarios that may be occurring between the sea water and Majimoto hot springs water, Chloride-Quartz Geothermometer Enthalpy diagram, comparative K/Mg vs. K/Ca plot and piper diagram were used. The results of the Chloride-Quartz Geothermometer Enthalpy diagram indicate that there exist two different mixing scenarios, one seen by the Bogoria waters and the Majimoto waters. High chloride Majimoto waters appear to lie on different mixing lines with the Bogoria waters. The original Majimoto hot springs water and the recalculated Majimoto springs water indicate a close

relationship. It appears that the original Majimoto are being diluted to form the recalculated Majimoto springs. This indicates that the sea water is the main cause of the elevated chloride levels. The results of the comparative K/Mg vs. K/Ca plot indicates that the Majimoto waters plot close to the sea water confirming the close association they have with the sea water. These results also confirms that the Majimoto hot springs waters are slightly immature and are either mixed or part of a flow-through type convective system. The position of the sea water is far from full equilibrium line close to the ultramafic dissolution line suggesting that the sea water represents a solute system far from any equilibrium involving minerals likely to control fluid chemistry in the geothermal systems. Further the piper diagram indicates two types of waters. The NaCl type of water indicated by the Majimoto springs which is consistent with sea water and the NaHCO₃ type of water shown by the Bogoria waters. These results therefore indicate that there is a relationship between the Majimoto springs water and the sea water. It also suggests that sea water is a component of the chemistry of Majimoto springs.

Chapter 6

6. Conclusions and Recommendations

6.1. Conclusions

3% of sea water is found in the Majimoto spring. The Cl-SO₄-HCO₃ ternary diagram indicates that the sea water did not affect maturity of hot springs waters. The Cl-Li-B ternary diagram was also used to support this conclusion whose results indicate a close relationship between the original Majimoto hot springs water and the sea water. The Na-K-Mg-Ca diagram results indicate that the original hot springs waters have a progressive change in chemistry towards the sea water as opposed to the recalculated chemistry which indicates a progressive change in chemistry away from the sea water.

Na-K-Mg ternary confirms that sea water indeed affects degree of hot springs water, whereby, contaminated hot springs water is partially equilibrated compared to uncontaminated hot springs water which is equilibrated.

The Chloride-Quartz Geothermometer Enthalpy diagram indicate that there exist two different mixing scenarios, one seen by the Bogoria waters and the Majimoto waters while the comparative K/Mg vs. K/Ca plot indicates that the Majimoto waters plot close to the sea water confirming the close association they have with the sea water.

6.2. Recommendations

I recommend further work involving a numerical model to investigate the occurrence of sea water intrusion in Majimoto to be carried out in order to support and validate the existence of sea water intrusion in Majimoto hot springs.

More studies involving hydrogeochemical processes that may accompany sea water intrusion into these hot springs should be done in order to determine if hot spring salinization is due solely to the mixing of hot spring water and sea water or if there are other hydrochemical processes involved that modify the theoretical hot spring-freshwater mixture.

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