# Geothermal activities in Rwanda: Hydrogeochemical characterization of geothermal waters and geothermometry applications

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**Abstract:** Prospecting studies indicate that Rwanda has a potential capacity to generate geothermal energy in the volcano-tectonically active zones of the East African Rift System (EARS). Two typical regions, Gisenyi and Mashyuza, were re-evaluated for the geothermal potential in Rwanda, where the hot springs were of Na-HCO<sub>3</sub> type waters. Geothermometers were applied to estimate subsurface temperatures of Gisenyi and Mashyuza springs and their suitability were discussed using Na-K-Mg diagram. In contradiction to previous studies, the results showed that only K-Mg geothermometer provided reliable estimations for Gisenyi and Mashyuza prospects for which reservoir temperatures are too low for energy production.

## Keywords: Geothermal water; Rwanda; Hydrogeochemistry; Geothermometers

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# 1. Introduction

Chemical characteristics of fluids provide useful geothermal details on the mineralogy of reservoir and describe the processes that contribute to chemical change of thermal waters during their ascent (Asta et al., 2012). Additionally coupled with the geochemical prospecting of natural thermal systems, the potential of geothermal areas can be evaluated correctly whether to be used as possible energy sources.

The geologic and geotectonic backgrounds of East African Rift System (EARS) in which Rwanda lies (western rift branch), suggested potentials for geothermal exploitation (Hochstein, 2005) and large seismic, tectonic and volcanic activities often well expressed on both eastern and western rift branches (Pürschel et al., 2013: Delelande et al., 2011;

Chorowicz, 2005). The hydrothermal manifestations in EARS are associated with Quaternary volcanism and faulting (Curewitz and Karson, 1997) where continental axial rift zones present high vertical heat flow (Hochstein, 2005; Omenda, 2005).

In Rwanda the Geothermal Energy Association estimated the geothermal energy potential ranging from 170 MW to 340 MW (Safari, 2010). The ongoing geothermal reconnaissance in Rwanda also revealed the geothermal energy potential up to 740 MW (Onacha, 2011).

Various studies (GoR, 1983; GoR, 2006; GoR, 2009) have been carried out to ascertain the potential of geothermal in Rwanda. Due to the intensive volcanic activities in the EARS, the existence of geothermal prospects is believed to be harvested

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Rwanda. for energy purposes in Preliminary surface extensive investigations were carried out in the 1980's at hydrothermal springs by the French Bureau of Geology and Mines (BRGM) (GoR, 1983). In the frame of the BRGM studies more than ten hot springs have been mapped in the Northwestern Southwestern and Rwanda. The results of the BRGM study suggested drilling sites in the southwest (Mashyuza) and northwest (Gisenyi) were as sites for geothermal energy development with estimated reservoir temperatures above 100°C (Namugize et al., 2013). A second assessment for two geothermal sites (Gisenvi and Mashyuza) was carried out by Chevron in 2006 (GoR, 2006). indicated that Chevron reservoir temperature in Mashyuza and Gisenyi could be in excess of 150°C. In 2008, the Germany Institute for Geosciences and Natural Resources (BGR), in collaboration with Kenya the Electricity Generating Company (KenGen), the Spanish Institute for Technology and Renewable Energies (ITER) and the Icelandic Geo Survey (ISOR) investigated surface studies in the Gisenyi, Karisimbi and Kinigi areas (GoR, 2009). The results from ITER study predicted a high geothermal temperature system (>200°C) on the southern slopes of Karisimbi volcano. Later in 2009, additional geoscientific surveys and baseline environmental impact assessment were carried out in the Karisimbi Prospect (Namugize et al., 2013). However, all of the assessments geological and geochemical on situations are still sparse, inconclusive and in addition contains significant errors in the interpretation of the data. (GoR, 2009). For example the interpretations using ternary Na-K-Mg as studied by GoR (2006) can only be

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applied to fully or significantly (cation-) equilibrated thermal waters while data points clearly appeared in the immature water field. As consequence, the temperatures calculated by previous studies seem to be erroneous and mis-interpreted.

To evaluate the geothermal energy series potential, a of empirical geothermometric models have been developed during the past decades such geothermometer functions as to subsurface estimate reservoir temperatures using chemical data (Fouillac and Michard, 1981; Fournier and Truesdell, 1973). Thereafter, the well known Na - K - Mg<sup>1/2</sup> ternary diagram is used to compare the of suitability different geothermometers (Giggenbach, 1988).

The aim of the present study is to revaluate the hydrogeochemical characterization of geothermal waters in Rwanda and to explore the appropriate geothermometric applications for better interpretations of deep reservoir temperatures.

# 2. Geodynamic situation of Rwanda

## 2.1. Geological background

Rwanda is located in the western branch of the EARS, a modern continental rift system where it consists of granites, phyllites, orthoquartzites, metaquartzites, pegmatites, migmatites, gneisses and micaschists of the Paleoproterozoic Ruzizian basement of the African craton. This basement is overlain by the Mesoproterozoic Kibaran Belt of Precambrian age, which covers most of the central Africa (Namugize et al., 2013; Kampunzu et al., 1986). The location of Rwanda in EARS is shown in Figure 1.

Basement geology of northern Rwanda is characterized by the Kibaran mid-Proterozoic mobile belt

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with local intrusions of anorogenic granites and syenites. The Kibaran, composed of folded and metamorphosed sediments, mainly schists and quartzites intruded by granites, covers most of Rwanda (Rogers et al, 1998). Cenozoic to recent volcanic rocks (Basalts) occur in the northwest and southwest. Some of these volcanics are highly alkaline and are extensions from the Virunga volcanic area (Namugize et al., 2013).



Figure 1: The location of Rwanda in EARS. WB means western branch; EB presents the

#### eastern branch

Tertiary and Quaternary sediments fill parts of the Western Rift in the western part of the country. The Virunga volcanic field is formed by large Pliocene-Pleistocene volcanoes (Muhabura, Gahinga Sabyinyo, Bisoke, Karisimbi, Nyiragongo and Nyamuragira (Tedesco et al., 2010). Virunga is in a large area of uplift associated with anomalously hot upwelling asthenosphere (Furman et al., 2004). Further, it is characterized by unusual silica undersaturated, ultraalkaline (K-rich) mafic volcanism that started erupting between 11 and 9 million years ago (GoR, 2009). The

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volcanism in Kivu volcanic province commenced in 8 million years with tholeiites followed by sodium lavas. Kivu volcanic province, along the border of Rwanda with Burundi and Democratic Republic of Congo where, comprises sedimentary basins made of border faults and its volcanism is linked to faulting (Furman, 2007; Furman and Graham, 1999).

# 2.2. Geothermal resources in Rwanda

Main geothermal resources distributed in Rwanda are shown in Figure 2. The Virunga volcanoes and the faults associated with EARS near Lake Kivu are two areas with potential geothermal exploitation that have been studied in Rwanda (Namugize et al., 2013; Rutagarama and Kamra 2007; GoR, 2006).



Figure 2: Simplified sketch showing main geothermal resources distributed in Rwanda

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The most prominent springs, with the highest temperature, are Mashyuza (to the south of Lake Kivu) and Gisenyi (north shores of Lake Kivu) (GoR, 2009). Gisenyi is located in the Virunga province dominated by active volcanism with magmatic eruption while Mashyuza prospect is located in a sedimentary graben delimited by faults in the South Kivu geologic province (Furman and Graham, 1999).

There are other minor geothermal resources in Rwanda that are less studied because the exit temperatures are very low for energy exploitations (Namugize et al., 2013; Onacha, 2011; Bahati et al., 2005).

# 2.3. Evaluation models

In order to ascertain the reservoir temperature in thermal systems, nine classical chemical geothermometer calculations were used such as quartz and amorphous silica (Fournier, 1977), chalcedony (Arnórsson et al., 1983), the cation geothermometers Na - K and K - Mg (Giggenbach, 1988) and Na - K - Ca (Fournier and Truesdell, 1973) , Na - K - Ca with Mg corrections (Fournier and Potter, 1979) and Na-Li(Fouillac and Michard, 1981).

Based on mineral-solution exchange, ionic solute geothermometers were also derived on equilibrium reactions between hydrothermal minerals and the aqueous solution under reservoir conditions. The decrease of Na/K ratio in thermal water with increasing temperature leads to an empirical correlation named Na-K geothermometer, the model was designed by Giggenbach (1988).

At the same time, Giggenbach (1988) observed the Mg content of thermal waters dependence on temperature was attributed to the equilibration of Mgbearing minerals and geothermal liquids.

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The empirical Na-K-Ca function was derived by Fournier and Truesdell (1973), assuming two different exchange mechanisms; Na-Ca-Solid exchanging with K<sup>+</sup> and Ca-K-Solid exchange with Na<sup>+</sup>.

Thereafter, due to the high partial pressures of carbon dioxide, the occurrence of exchange reactions involving Mg and calcite precipitation might lead to overestimation of the equilibrium temperature. Therefore the model only involving the Na-K-Ca function could provide erratic results below 200°C, which prompted Fournier and Potter (1979) to propose a quite complex Mg-correction with Na-K-Ca-Mg function.

A questionable geothermometer based on Li/Na ratio was developed by Fouillac and Michard (1981). Its utilization is still limited due to variable fraction of Li-end memeber in the solid mixtures taking part to the exchange reactions.

# 3. Results and discussion

#### 3.1. Hydrogeochemistry

The hydrogeochemical data of geothermal waters of Gisenyi and Mashyuza were compared in Table 1 where three of seven total water samples were from Gisenyi (G) hot springs and four from Mashyuza (M) prospects. The identified samples were labeled with site and date, for example G-1-1983 means the first hot water sample that was taken in Gisenyi in 1983 and M-2-2006 stands for the second hot water sample from Mashyuza in 2006.

**Table 1:** Hydrochemical data composition of waters from Gisenyi and Mashyuza geothermal fields (GoR, 2006; GoR, 1983) (unit:  $mg \cdot L^{-1}$  except for pH)

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	T OC		<b>N</b> 7		NT /17	G		0	n		CI:OA	CI	004	HCOA	TDC
SampleID	T°C	рН	Na	K	Na/K	Ca	Mg	Co	В	Lì	S102	CI	804	нсоз	TDS
G-1-2006	70.6	7.00	518.8	39.8	13.0	36.40	11.10	n.a	0.55	0.42	58.50	236.80	62.10	1137.3	2101.90
G-1-1983	70.6	6.69	531	41.06	12.9	37.99	11.39	5.2	n.a	0.41	109.95	233.99	54.00	1122.7	n.a
G-2-1983	31.7	6.47	528.7	40.67	13.0	37.79	11.12	5.2	n.a	0.41	105.75	233.99	44.00	1122.7	n.a
M-1-2006	33.0	7.00	291.2	45.30	6.4	89.50	51.80	n.a	1.18	0.93	50.20	141.00	50.50	1115.8	1836.78
M-1-1983	41.8	6.45	287.4	45.36	6.3	76.95	51.77	2.9	n.a	0.90	84.72	120.89	48.03	1049.5	n.a
M-2-2006	47.0	6.50	307.8	48.00	6.4	76.00	55.00	n.a	1.07	0.96	48.30	137.90	55.30	1122.7	1855.00
M-2-1983	54.2	6.25	298.8	47.31	6.3	72.94	53.96	3.5	n.a	0.95	186.86	127.98	46.01	1061.7	n.a
	0 1.2	0.20	_>0.0	.,	0.0		22.70	0.0		0.70	100.00	12.190		1001.7	

n.a: not analysed

It is obvious there was no significant change between 1983 and 2006 except silica content. In general, pH values ranged from 6.25 to 7.00 and temperatures from 33 °C to 70.6 °C. There are several reasons for SiO<sub>2</sub> variation. One was probably due to different sampling and storage techniques which were used; another was due to natural variations over time. addition, the intense tectonic In earthquakes and volcanic eruptions that occurred during this period might have played a significant role on SiO<sub>2</sub> content (Mavonga et al, 2010), which was also reported by GoR (2009) about the relationship between the active tectonics and the ascent of geothermal waters in Rwanda.

In general, Gisenyi and Mashyuza exhibited higher concentrations of HCO<sub>3</sub>, Na, and SiO<sub>2</sub> while lower contents of B and Li. Compared with the hot springs in Gisenyi, the geothermal waters in Mashyuza were enriched considerably in Mg but depleted in SiO<sub>2</sub>, suggesting that

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Mashyuza is significantly lower temperature resource than Gisenyi.

Figure 3: Cl-SO<sub>4</sub>-HCO<sub>3</sub> ternary diagram in Gisenyi and Mashyuza geothermal waters

This is ascribed to Mg content of thermal waters dependence on temperature attributed to equilibration of Mg-bearing minerals and geothermal liquids (Giggenbach, 1988). Cl-SO<sub>4</sub>-HCO<sub>3</sub> ternary diagram is shown in Figure 3. It was postulated that the in Gisenvi and water ancient Mashyuza was from geothermal systems being cooled down or from the peripheries of geothermal

systems due to the enrichment of bicarbonate in cold groundwater.

Finally, seen from Table 1, the Na/K ratio in thermal waters from the study areas were around 13 for Gisenyi and 6 for Mashyuza, suggesting both of them were associated with the upflow structures. Because the Na/K ratio is controlled by temperature dependent mineral fluid equilibria, the water with relatively low Na/K ratios (less than15)

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prefer to reach the surface rapidly (Gemici and Tarcan, 2002). The constant Na/K ratios for each prospect samples may also suggest a homogenous fluid at depth in both Gisenyi and Mashyuza hot springs.

The Piper diagram of Gisenyi and Mashyuza hot springs was plotted in Figure 4. It shows that the hot springs in Gisenyi and Mashyuza were of Na-HCO<sub>3</sub> type waters due to the domination of bicarbonate and Na. This is consistent with chemical characteristics of most of geothermal waters in EARS, where they present a higher linear correlation of bicarbonate and major mobile cations especially Na (Delalande et al., 2011).



Figure 4 : Piper diagram of Gisenyi and Mashyuza hot springs. 1-CalciumMagnesium Sulphate; 2-Sodium Chloride; 3-Sodium Bicabornate Sulphate; 4-Calcium Magnesium Bicarbonate; A-Maganesium; B-Mixed zone; C-Calcium, D-Sodium Potassium; E-Sulphate; F-Mixed zone; G-

Chloride; H-Bicarbonate

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Moreover, alkalis (Na<sup>+</sup> and K<sup>+</sup>) exceeded alkaline earth metals (Ca<sup>2+</sup> and Mg<sup>2+</sup>) while weak acids ( $HCO_3^-$  and  $CO_3^{2-}$ ) dominated strong acids ( $Cl^-$  and  $SO_4^{2-}$ ). Therefore, the depletion of (Ca + Mg) and the enrichment of (Na + K) in thermal waters also explained the interaction of  $CO_2$  with water and rock (Fara et al., 1999). chemical composition of water at depth is preserved during their ascent.

### *3.2. Geothermometry*

The comparison of estimating subsurface temperatures in hot springs was shown in Table 2 according to the equations (1)-(9) called also geothermometers assuming that the

 Table 2: Subsurface temperatures (in °C) of the hot spring waters in Gisenyi and

 Mashyuza geothermal fields

SampleID	Quartz <sup>(1)</sup>	Quartz <sup>(2)</sup>	Chal <sup>(3)</sup>	Amorph <sup>(4)</sup>	Na- K <sup>(5)</sup>	K- Mg <sup>(6)</sup>	Na-K- Ca <sup>(7)</sup>	Na-K- Ca- Mg <sup>(8)</sup>	Na- Li <sup>(9)</sup>
G-1-2006	109.3	109	80.7	-7.6	212	99	181	72.3	97.7
G-1-1983	142.5	137.2	114.4	21.7	212.5	99.6	189	74.4	95.4
G-2-1983	140.3	135.3	112.2	19.7	212	99.7	188.6	75.4	95.6
M-1-2006	102	103	73.3	-13.8	270.2	82.4	201.6	28	182
M-1-1983	128	125	99.7	8.9	271.6	82.5	212	24.4	180.5
M-2-2006	100.2	101	71.5	-15	270.4	83	204.5	21.5	180.2

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M-2-1983	121.8	119.7	93.3	3.3	272	83	213.4	22	181.6
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(1) Fournier (1977) ; (2) Fournier

 (1977) ; (3) <u>Arnórsson</u> et al.
 (1983) ; (4) Fournier (1977) ;
 (5)Giggenbach(1988) ; (6)
 Giggenbach (1988) ; (7)

 Fournier and Truesdell (1973);

 (8)Fournier and Potter (1979);
 (9) Fouillac and Michard (1981)

The Na - K - Mg<sup>1/2</sup> ternary diagram afterwards was plotted to evaluate the suitability of different geothermometers in Figure 5, which was applied for solute geothermometers to characterize water parameters (Michel et al., 2002; Gemici and Tarcan, 2002).



Figure 5: Na - K - Mg<sup>1/2</sup> ternary diagram of Gisenyi and Mashyuza hot springs (Sqr: square root)

It can be used to indentify whether the hot waters arrived the full or partial equilibrium with rock at given temperatures (Giggenbach, 1988). Seen from the Figure 5, the hot springs in Gisenyi and Mashyuza were closely to immature waters (shallow/mixed water) due to their shift towards Mg<sup>1/2</sup> apex. For the samples plotting in the immature waters field, the

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application of Na - K - Ca, Na - Kan quartz geothermometers, and indeed any type of cation geothermometers, is doubtful. The interpretation of the temperature predictions of such waters should be made cautiously (Giggenbach, 1988).

Na-K geothermometer worked out reservoir temperatures about 212°C for Gisenyi and 270-272°C for Mashyuza The Na - K - Cawaters. geothermometer, developed to eliminate the effect of Ca contents, yielded temperature estimates of 181-188.6°C for Gisenvi and 201.6-213.4°C Mashyuza for waters. These temperatures were lower than those estimated by Na-K geothermometer but still higher than that by quartz and chalcedony geothermometers (seen in Table 2). The results showed the Na - K - Cageothermometer has small differences from Na-K geothermometer for Gisenyi hot

springs. Thus, it was concluded that the low Ca concentrations have no significant influence on the applied geothermometry for Gisenyi hot springs. However, a slight influence of Ca content was observed in Mashyuza when Na - K - Cawaters geothermometer was applied, which was proved in Table 1 where the content of Ca in Mashyuza hot springs ranged from 73 to 89 mg·L<sup>-1</sup> while Gisenvi waters presented less than half of it  $(36-38 \text{ mg} \cdot \text{L}^{-1})$ . Thus, only Na - K - Ca geothermometer could be applied in Mashyuza waters when taking into account the Ca influence as the Na-K geothermometer has been reported to yield unreasonably high temperature estimate for waters having high Ca contents (Fournier and Truesdell, 1973).

The K-Mg and Na - K - Ca - Mggeothermometers suggested subsurface minimum reservoir temperatures or

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temperatures that were too low which corresponds to immature water as shown in Figure 5. These temperature results (77.3-99°C for Gisenyi and 21.5-83°C for Mashyuza hot spring waters) probably resulted from the faster re-equilibration of K-Mg during the upflow of the water, as well as the mixing process with relatively Mg-rich immature waters (Michel et al., 2002). For example the computed temperatures

using Na - K - Ca - Mg geothermometers in Mashyuza yielded temperatures lower than measured surface ones. The temperature estimations using Na/Li model were also low, especially in Gisenyi waters because the auxiliary geothermometer depended not only on temperature but also on the fluid salinity and the geologic setting.

The quartz geothermometers model yielded reservoir temperatures between 109-142°C for Gisenyi and 101-125°C for Mashyuza spring waters. Quartz geothermometry revealed remarkable differences in temperatures when other silica compared to geothermometers (amorphous silica and chalcedony) due to the control of the quartz solubility (Fournier, 1977). For example amorphous silica geothermometers yielded temperatures lower than the discharge temperatures.

Therefore, estimating when subsurface temperatures, the locations of the springs emanating from the old basement rock were more likely to have equilibrated with quartz than chalcedony. Furthermore, it is known that mixing geothermal fluids with immature waters has a negative effect the reliability of the silica on goethermometers. Ratios instead of absolute concentrations of the ions were used to estimate temperature because cation geothermometry has less sensitivity to mixing and re-

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equilibration processes during the upflow (Pürschel 2013). et al., Temperatures calculated by Na - K - Ca, Na - K, quartz geothermometers, and indeed any type of cation geothermometers (except K-Mg) are erroneous in Mashyuza geothermal prospect, as it was closer to Mg vertex in Na - K -  $Mg^{1/2}$  diagram and Ca influence was of great extent. Thus. only K - Mg solute geothermometric models provided more accurate reservoir temperature estimations in the studied waters of Gisenyi and Mashyuza contrarly to the previous misinterpretations which used geothermometers only requiring cation-equilibrated thermal waters.

#### 4. Conclusions

The thermal waters in the western part of Rwanda are of immature water type based on the  $Na - K - Mg^{1/2}$ diagram and they are observed to be of Na-HCO<sub>3</sub> type waters. Combining the results of the two different geothermal sub-regions, it has been observed that heat-generating low capabilities throughout Gisenyi and Mashyuza areas less than 100°C according to the estimation K-Mg using geothermometer model which is the only one to be used in fast mixing immature water. The calculated temperatures are less than the previous estimates (GoR, 1983; GoR, 2006), for the same thermal systems. There is therefore no evidence for deep thermal the fluids beneath Gisenyi and Mashyuza thermal spring areas with inferred temperature of 200 to 220°C as they have been interpreted in previous reports. Both Gisenyi and Mashyuza springs contained lower concentrations of Mg and higher concentrations of silica, indicating that they are likely originate from lower temeperature reservoirs.

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Given Gisenyi and Mashyuza thermal waters do not attain equilibrium, the evaluation of equilibrium temperatures may not be applicable and the results obtained by the cation geothermometers should be taken into account as doubtful. It is recommended that enthalpy mixing models, isotope and trace element and thermodynamic saturation state studies should be applied as further approach to predict the subsurface temperature accurately in both Gisenyi and Mashyuza prospects.

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