Proceedings World Geothermal Congress 2020+1
Reykjavik, Iceland, April - October 2021

Application of Cation Geothermometry: The Case of Butajira Geothermal Prospect, Ethiopia

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Keywords: Geothermometry, Butajira, hot springs

ABSTRACT

Butajira geothermal prospect is found in the Central Main Ethiopian Rift (CMER) near the Western rift escarpment, where thermal manifestations such as hot springs are aligned in a NNE/SSW direction and surface temperatures reaching up to 86◦c are located. The main objective of this study is to characterize the reservoir of the geothermal system in Butajira by estimating the sub-surface temperature using Cation geothermometry. As a result, sub-surface temperature exceeding 150°c is obtained using Na-K geothermometer, in which the prospect can be regarded as high enthalpy geothermal prospect.

1. INTRODUCTION

The CMER is in a kind of transition phase, where localized strain is shifting from the margins toward the rift floor (Agostini et al, 2010) and rift margin geology is dominated by volcanic rocks of the Tertiary Period (WoldeGebriel, G. et al, 1990). Despite the occurrence of high enthalpy geothermal fields along the axial rift in Ethiopia, Butajira prospect is located 150km Southwest of Addis Ababa along the foot of the Western rift escarpment. It is found under the Southern Nation, Nationality and People Regional state (SNNPR), within the Silti zone. It is accessible via two-ways, one is through Ayer Tena in Addis to Tiya, Kela, Butajira and Silti, while the other is from Addis to Debre Zeyt, Ziway, Butajira and Silti.

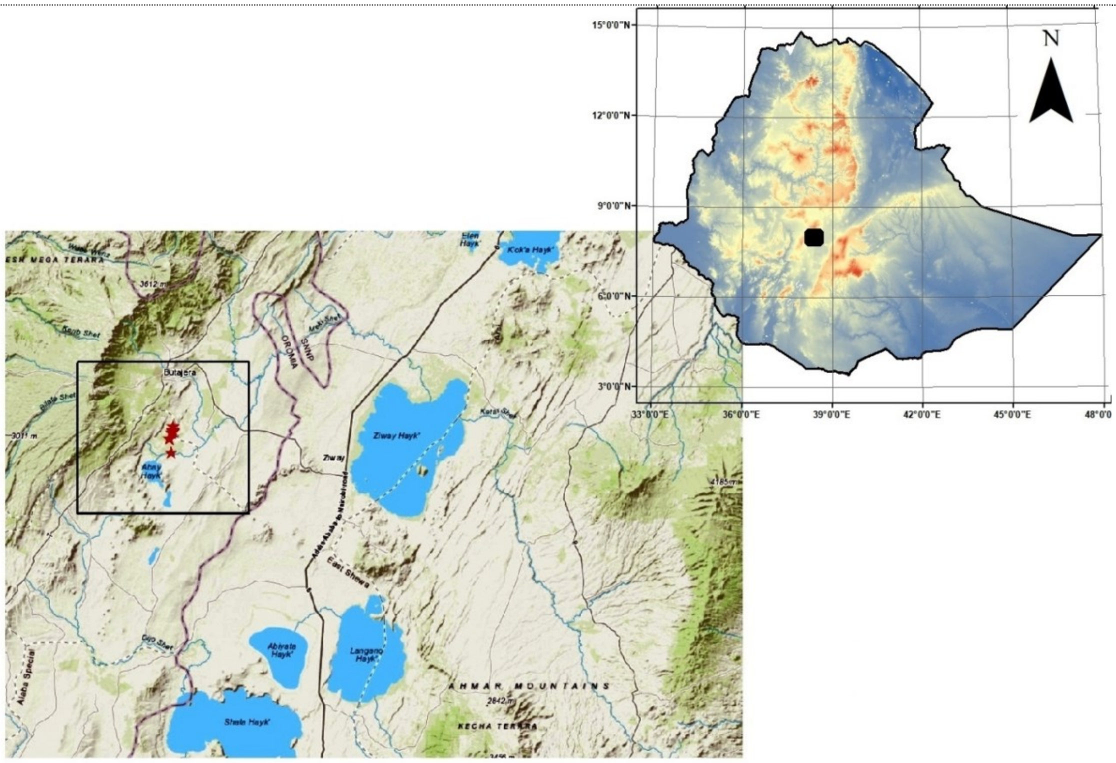

Figure 1. Location map of Butajira geothermal prospect in a black box where red stars show the site of thermal manifestations.

2. LITERATURE REVIEW

There are quite different works conducted within the Main Ethiopian Rift (MER). The evolution of rifting, propagation and localization of active deformational zones has been investigated using geological, geochemical and geophysical approaches. Several geological units of the MER, Quaternary volcanism, age of the associated tectonic structures, and their orientation was discussed by pioneer geoscientists like Mohr (1962). In this study, recently published articles are included as well.

2.1. Geological and Geochemical Overview

WoldeGabriel. G., et al (1990) managed to do petrography and K/Ar dating from rocks exposed in both sides of the rift escarpments and provides the stratigraphic chronology of the CMER. According to the chronology they put from Oligocene up to recent, there have been six sequences of volcanism, they tried to classify and show the development of the rift in two different phases. The existence of recent basaltic lava flows in Butajira, East Ziway and Southern Shala associated with fissural scoria cones are reported also by Di Paola (1973). Various base and precious metals like chromium and gold, more than 21ppm and 0.06ppm respectively, were reported to be found around Butajira and its surrounding areas, from geological and geochemical approaches (GSE, 2010). Agostini et al (2011) conducted ^{14}C radiometric dating on rocks that are affected by faulting from both rift margins and shows that the youngest border faults are to be 30ka for the western and 7-9ka for the eastern escarpment. Keranen and Klemperer (2008) indicate that rift propagation is controlled, and largely dependent on, pre-existing structures. They concluded that rift development is credited by tectonical structures at earlier times and has been recently dominated by magmatism.

From fault kinematics, petrology, and satellite image analysis Bonini et al (2005) suggested that rift propagation is towards the south. They argue that after the initiation of the Southern Main Ethiopian Rift (SMER) and Northern Main Ethiopian Rift (NMER) from 20-21Ma and 11Ma respectively, the deformation ceased to continue further North probably due to pre-existing transversal structures. From exposed basement rock located in the CMER, Tsegaye Abebe et al (2010) conducted apatite fission tracking and emphasized the model proposed by Bonini et al (2010), confirming the age of CMER to be younger than 8Ma. Structural and geological, as well as GPS data analysis in the CMER, reveals that both faulting, provoked by magma, and pre-historic tectonical structures, caused by earthquakes, have been accounted for being responsible for strain accommodation (Pizzi et al., 2006).

From geochemical perspective Rooney et al (2007) reports that the magmatic system is better developed along the Wonji Fault Belt (WFB) than underneath the Silti Debre Zeit Fault Zone (SDFZ). Moreover the fractionation depth of the magma in eastern escarpment is at shallower depth while magmas at SDFZ are from deeper fractionation depth (Rooney, 2010). He also conclude that there is a clear relationship between tectonics and magmatism from major and trace element analysis on the basaltic lavas from the recent structure of WFB and SDFZ. Xenoliths inclusion in the lavas of Butajira has been shown to contain Al- augite which is widespread along the youngest deformation zones of SDFZ and WFB, implying the event of dyking in to the crust to a depth of 30km (Rooney et al., 2005). Using major and trace element isotopic analysis on the very recent (<1Ma) basaltic lava fields of Debre Zeyt and Butajira area, Rooney et al (2012) concludes that there is clear discrepancy in the original source of the isotopes analyzed. They insist that there is mixing between the asthenospheric upper mantle, the diverging continental lithosphere as well as contribution from deep seated plume. From radiometric, petrographic, and structural data Tsegaye Abebe et al (1998) suggests on the volcanism of Yerer Tulu Wellel Lineament (YTVL), E-W trending trans-tensional structure, to be controlled by both regional structural effect and by anomalous heat from the MER.

It has been shown that there are variations in the evolution of highly differentiated rocks and to take care when using Sr isotope methodology (Deniel, 2009). The reason for the observed discrepancy of rock compositions from Gedemsa Volcano were petrochemicaly analyzed (Peccerillo et al., 2003). They have interpreted the variation by saying that silica rich evolved products can be fractionated from mafic magmas, and explain the paucity of intermediate rocks due to short temperature interval associated with the collapse of the caldera. Hutchison et al (2016) also indicates the genetical origin of the rocks from Gedemsa to be predominantly affected by fractionation processes. Fractionation process has been reported to play the major role in producing variation in composition of rocks erupted from the same vent, as it is observed in the petrogenesis from lavas of pre- and post-caldera formation of the Fentale Volcano (Gibson, 1972). Minissale et al (2017) conducted geochemical investigation in the SMER using $^{3}He/^{4}He$ isotopic ratio and geothermometery application in Northern Abaya and reveals both the equilibrium temperature of the reservoir and the source of origin for the thermal fluids. The low helium isotopic ratio of 2.3Ra calculated for Butajira hot springs is interpreted to be caused by the contribution of radiogenic helium added from an evolved shallow magma chamber (Sinetebeb et al., 2020).

2.1.1 Geophysical Overview

The contribution of mantle upwelling and the effect of Mid Oceanic Ridge (MOR) along with the variation in the physical properties of several types of rocks is said to be the major cause of rifting in East Africa, as shown in the spherical shell stress model of Min and Hou (2018). Whaler and Hautot (2006) provide resistive structure of the crust beneath Boset volcanic complex and revealed the presence of a magmatic chamber at 20km depth by using audio-frequency Magneto-Telluric measurements. Cornwell et al (2006) confirmed in their density model beneath Boset volcanic center that there is mafic intrusion at around 20km depth. Velocity modeling conducted along a profile that transects the MER through Boset Volcano suggests higher velocity values to be found within the rift, presumably due to magmatic intrusions than in the plateaus (Mackenzie et al., 2005). Seismic refraction method conducted in the NMER showed that the P-wave velocity increases under the rift axis, rather than underneath the margins (Maguire et al., 2006).

Bastow et al (2000) insists for the cause of strain accommodation in NMER to be predominantly magmatic intrusion as observed from tomographic inversion of P and S wave data. Furthermore, using geodesy combined with fault slip inversion data Ameha Muluneh et al (2014) concludes that, left lateral transtensional components are responsible for the propagation and evolution of the Ethiopian rift. They have suggested the sigmoidal shape of the Quaternary WFB as evidence. Recent (MT) resistivity models conducted around Aluto suggests that the cause of unrest in Aluto is not driven by the action of shallow magmatic system (Samrock et al., 2015). They rather concluded the occurrence of substantial melt at relatively shallower depth to be found along SDFZ.

3. ANALYTICAL TECHNIQUES

Six water samples have been collected from hot springs near Ashute village. The criterion for selecting the location for sampling is based on spring temperature. Geothermometers such as cation geothermometer are used for temperature estimation of the geothermal reservoir. The highest surface fluid temperature available has been taken. Clear hot springs that are not mixed with cold ground water were selected as much as possible. All the samples were filtered using 0.45 μm membrane and stored in a 250ml polyethylene bottles. Each sample was acidified with 2ml of HCl. The concentration of the acid is 0.02 since 2mg of powder HCl was stirred in 100ml of water. The samples were analyzed in the laboratory of chemistry at Addis Ababa University.

4. THEORETICAL BASIS OF GEOTHERMOMETRY

Geothermometry is widely accepted as reliable method in estimating subsurface reservoir temperature (Wishart, 2015, Arnorsson, 2000). Fournier (1977) classifies chemical geothermometers as being qualitative and quantitative. The qualitative geothermometers are mostly helpful for geothermal fields that are poorly constrained and where no appropriate data is readily available. Mercury from stream sediments and volatile elements from the soil can predict the existence of old thermal manifestations (Fournier, 1977). The constituents of geothermal fluids are derived either by dissolution of primary minerals, or from precipitation of secondary minerals (Arnorsson, 2000). These geothermometers provide numerical values and are regarded as quantitative geothermometers offering the least expected reservoir temperature (Fournier, 1977).

Geothermometers can also be classified as solute, gas, and isotope geothermometers (Arnorsson, 2000; Karingithi, 2009). Out of the major processes that occur when geothermal fluids rise to the surface, one is losing heat by conduction. Conductive cooling does not always change the chemical composition of the rocks. However, it will certainly influence the rate of saturation for minerals, either by dissolution or by precipitation. The other process that changes the composition of the fluid is adiabatic cooling, which occur during degassing by concentrating the solute in favor of steam loss (Arnorsson, 2000). In conditions where sub surface temperature is below the boiling temperature of the atmosphere, the temperature of the water that is coming out can be thoroughly considered as the aquifer temperature. If the formation temperature exceeds the atmospheric boiling temperature, then adiabatic cooling of the water will occur (Fournier, 1977).

There are assumptions that require consideration in using geothermometers like for instance there is no conductive cooling and the system is considered to be adiabatic (Arnorsson, 2000; Karingithi, 2009; Murithi, 2012). According to Wishart (2015), there are several other assumptions to be considered in dealing with geothermometry such as, the abundance of mineral constituents ascending to the surface vary rapidly, and most importantly the chemical reactions governing the mineral species must be temperature dependent at specific depth. The other assumptions that require consideration is that there is no mixing with cold ground water and no re-equilibrium shall occur during ascent of geothermal fluid to the surface (Fournier, 1977).

There are two reactions which are exclusively dependent on temperature that governs the fundamental principle behind the application of geothermometers, namely solubility and exchange reactions (Fournier, 1977). When subsurface temperature increases above 150°c equilibrium between minerals, solute can always be maintained. When the fluid migrates to the surface, degassing and dilution are among the major factors that led the fluid to not be in a state of equilibrium (Wishart, 2015). There are two ways for calibrating geothermometers. One can be retrieved by doing experiments that determine equilibrium constant, called theoretical, and the other is from associating concentrations with their respective aquifer temperature (Arnorsson, 2000).

Reservoir temperature estimation is given in accordance with depth Wishart (2015). Although equilibrium conditions can only occur within the reservoir, the application of geothermometry can at least tell the temperature at which equilibrium was last maintained (Arnorsson, 2000). Many equations have been devised by different scientists. An equation for a typical geothermometer reflects the temperature condition at which equilibrium was last achieved (Arnorsson, 2000; Battistel et al., 2014).There is a range of temperature where a typical mineral assemblage can be formed, so knowing the mineral assemblage can tell us at what equilibrium temperature that typical arrangement exists (Wishart, 2015). In order to identify an equilibrated system from non-equilibrated, the application of various mineral equilibrium is essential (Arnorsson, 2000). The possibility of the rock to leach during interaction with the water has an influence on achieving state of equilibrium. This is because it has direct impact in deciding the concentration of dissolved indicator elements (Fournier, 1977). The original temperature, and the resident time of the water within the reservoir and its flow rate, play a great role for re-equilibrium to exist (Fournier, 1977). Powerfully rising fluid is less affected by conductive cooling than slowly rising water, which has considerable heat loses (Fournier, 1977).

4.1 Na-K geothermometry

Although it is not necessarily true, the assumption that the chemical constituents are preserved within the water is the basis for the application of chemical geothermometry. If equilibrium exists, ratio between cations can be used as geothermometer (Arnorsson, 2000, Fournier, 1977). Cation geothermometry, which is dependent on equilibrium ion reaction, especially the Na-K geothermometers, is suitable for temperatures over 180°c (WRC, 2013; Murithi, 2012).

Fournier (1977) proposed range of temperature from 100°c up to 200°c. The ideal place of deposition for feldspars is usually the up flow zone, since their solubility increases with increasing temperature they have the tendency to precipitate during heat loss from the fluid, either by boiling or through conduction (Arnorsson, 2000). The process occurring in aqueous solution between feldspars is called exchange reaction (Arnorsson, 2000). As equilibrium temperature changes, the ratio between indicator elements also changes (Fournier, 1977). Na-K geothermometer depends on the detachment of Na and K from the aluminosilicates (Arnorsson, 2000). The exchange reaction between Na and K is given below (after Arnorsson, 2000).

$$NaAlSi_3O_8 \text{ (albite)} + K^+ = KAlSi_3O_8 \text{ (K-feldspar)} + Na^+$$

Na-K geothermometer is widely accepted for estimating reservoir temperature for both felsic and mafic rock compositions (Arnorsson, 2000). It is well established, from previous researches, that the feldspars in low grade metamorphic rocks and hydrothermally altered rocks are microcline and albite respectively. Na-K geothermometer can provide reliable results for reservoir temperature above 100°c and for fluids with few calcium content (Karingithi, 2009; Murithi, 2012). Although factors such as fluid residence time in the sub-surface and temperature have effects in the estimation of reservoir temperature, Na-K geothermometer is still crucial, since Na and K respond very slowly to re-equilibrate after cooling (Arnorsson, 2000).

4.2 Water Geochemistry

Numerous hot springs in the Butajira field are aligned in a NNE/SSW direction following the WFB trend. Apart from determining the source of the fluid, the temperature of deep geothermal reservoir can also be provided numerically using molecular ratio (GSE, 2004). Among the common applications such as solute (water), gas and isotope geothermometry (Arnorsson, 2000), the water geothermometry is applied in this work. From various geothermometers, the Na/K geothermometer, which is considered as one of the most reliable geothermometers (Wishart, 2015, Fournier, 1977, Fournier, 1979) has been selected and used in this research. The results are shown in Table 1 and 2.

Table 1 Estimated reservoir temperature of six cation samples calculated using the equation (after Arnorsson et al., 1998)

ID No	Location in (UTM) 37N		Elevation in (m)	Surface temperature in (˚c)	Concentration of cations in (ppm)				Estimated subsurface temperature In (c)
	Easting	Northing			Na^{+}	K^{+}	Mg^{2+}	Ca^{2+}	
C-1	433580	885955	1824	85	251.482	9.3147	2.8672	0.0921	167.461
C-2	433555	885919	1820	86	241.479	9.9387	4.1446	1.6205	173.369
C-3	434326	886670	1819	84	143.753	0.5931	0.4552	5.8098	56.9100
C-4	432820	884392	1819	86	132.276	2.0848	5.201	8.8847	113.774
C-5	432877	884579	1808	79	218.992	5.5916	0.9026	2.3047	140.448
C-6	433389	885734	1820	69.7	167.23	5.131	2.9141	3.3968	153.037

Table 2 Estimated reservoir temperature of six cation samples calculated using the equation (after Fournier 1977)

ID No	Location in (UTM) 37N		Elevation in (m)	Surface temperature in (˚c)	Concentration of cations in (ppm)				Estimated subsurface temperature In (c)
	Easting	Northing			Na^{+}	K^{+}	Mg^{2+}	Ca^{2+}	
C-1	433580	885955	1824	85	251.482	9.3147	2.8672	0.0921	145.85
C-2	433555	885919	1820	86	241.479	9.9387	4.1446	1.6205	151.85
C-3	434326	886670	1819	84	143.753	0.5931	0.4552	5.8098	40.85
C-4	432820	884392		86	132.276	2.0848	5.201	8.8847	96.85
C-5	432877	884579	1808	79	218.992	5.5916	0.9026	2.3047	121.85
C-6	433389	885734	1820	69.7	167.23	5.131	2.9141	3.3968	133.85

5. ESTIMATION OF RESERVOIR TEMPERATURE

The temperature of the hot springs at the time of collection lies from 69˚c up to 86˚c. Some geothermometers may either overestimate or underestimate subsurface temperature, so comparison between various geothermometers is essential. Using Na/K geothermometer according to the equation proposed after Arnorsson et al (1998), and using the equation of Fournier (1977), reservoir temperatures that range from 96˚c -151˚c, and temperatures ranging from 113˚c -173˚c respectively, is determined for Butajira hot springs. The water type is considered as Na-HCO_3-SO_4 as plotted in Figure 2. Among the six samples taken cat-ash 3 has been excluded from interpretation as the temperature estimated for the sub-surface is much lower than the measured surface temperature. Any sample whose estimated value is lower than the surficial value is not a representative sample (Yuce and Taskiran, 2013). This can be due to mistake during the acidification of the sample or during sample analysis. The samples are plotted as shown in Figure 2 in the Giggenbach triangular diagram to prove whether or not rock water equilibrium exists in the aquifer. All the samples except cat-ash 3 are plotted and lie in the partial equilibrium zone. This shows some kind of mixing with cold ground water at the surface. The result obtained from Na-K geothermometer can be taken as reliable, since it neither overestimates nor underestimates the reservoir temperature. Furthermore, partial rock water equilibrium has been shown in Figure 2. If all the samples lie in the immature zone and neither partial nor full equilibrium is maintained, then reliability in the result of the geothermometer will not be accepted (Yuce and Taskiran, 2013). However, the temperature of the geothermal reservoir is expected to be higher than the estimated value obtained from using both equations proposed by Arnorsson et al (1998) and Fournier (1977). This is because it is obvious that the fluid temperature will decrease from its original value by the time it reaches the surface (Arnorsson, 2000).

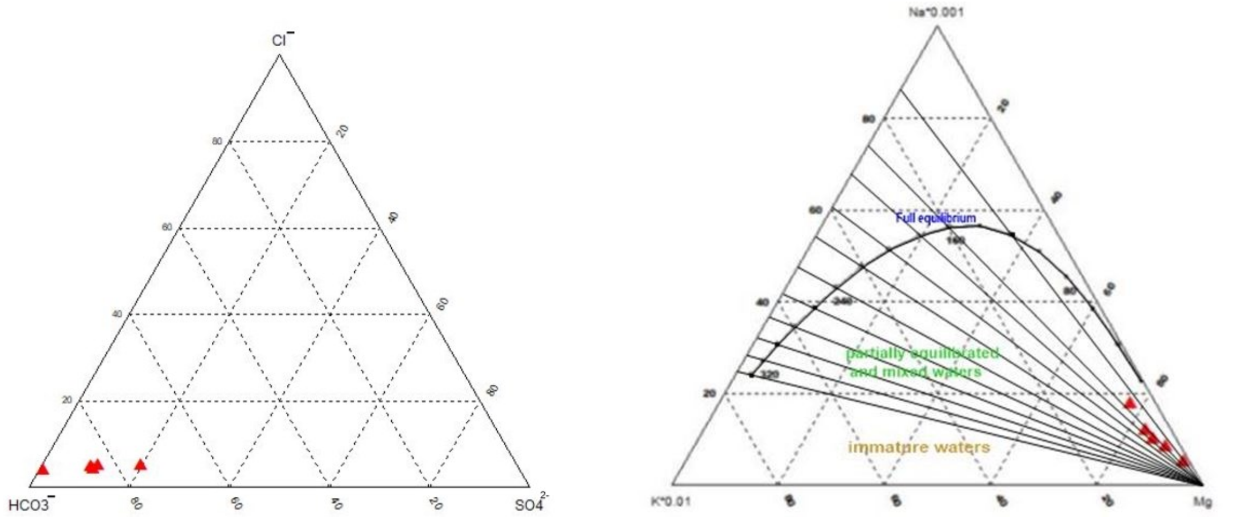

Figure 2. Ternary diagram with Butajira samples plotted close to the HCO_3 axes (left) and Na-K-Mg ternary diagram (after Giggenbach, 1988) where red triangles indicate Butajira samples plotted in the mixed and partially equilibrated zone (right).

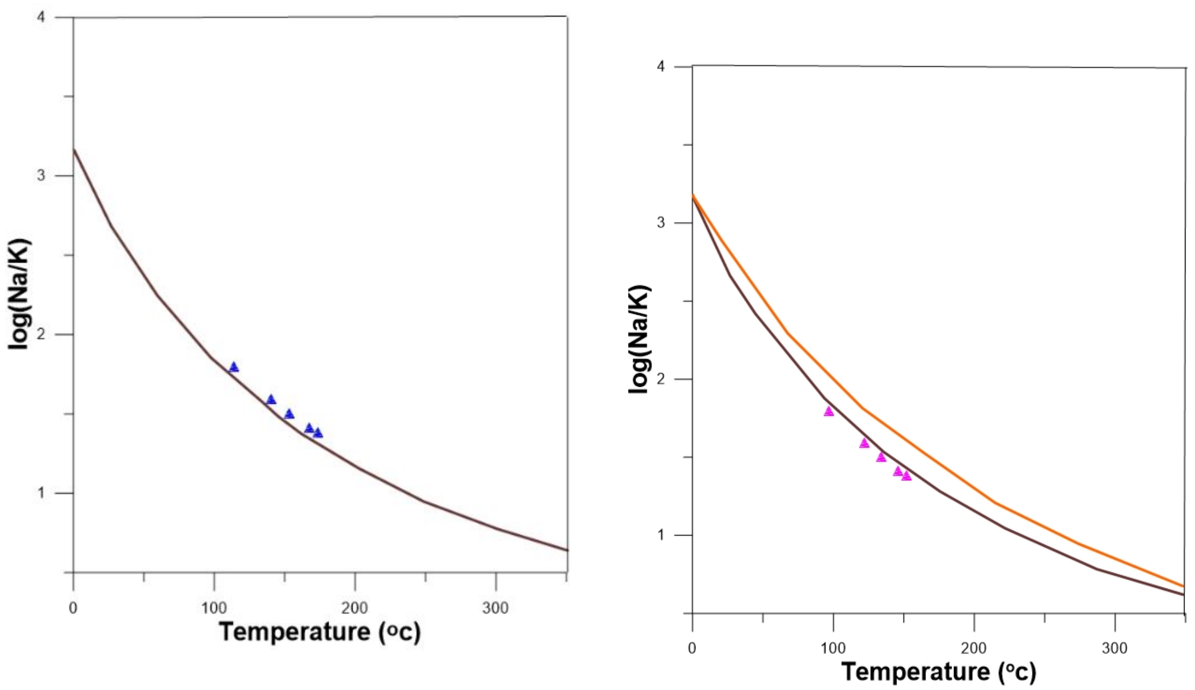

Figure 3. Temperature curve for the Na/K geothermometer (after Arnorsson, 2000) where the blue triangles representing Butajira samples calculated using the equation after Arnorsson et al 1998 (left) and the purple triangles calculated after the equation proposed by Fournier 1979 (right).

6. CONCLUSION

The average estimated reservoir temperature obtained from Arnorsson et al (1998) is 150◦c, while temperature estimated after Fournier (1977) shows 173◦c. Thus, the sub-surface temperature in Butajira geothermal field is at least certainly above 150◦c in temperature. The broad consistency of Butajira samples calculated both after the proposed equation by Arnorsson et al (1998) and Fournier (1979) is shown in Figure 3. In fact, the closeness of the value for the estimated temperature from the two equations gives reliability of the results obtained.

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