Fumarole Gas Geochemistry of Paka Geothermal Prospect, North Rift, Kenya

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ABSTRACT

Intense and widespread geothermal surface activity manifested in the form of fumaroles, hot grounds and hydrothermally altered rocks characterize Paka geothermal prospect. Geochemical investigation entailing sampling and analysis of steam discharges from selected fumaroles was carried out. Chemical results of fumarole discharges were used to predict the chemical characteristics of the geothermal reservoir as well as estimate subsurface temperatures. The fumarolic gases are CO_2-dominated with significant H_2 and CH_4 concentrations present. H_2S may have been lost during ascent of the fluids to the surface or possibly due to the generally low H_2S concentrations in the Kenya Rift. Reservoir temperatures in excess of 300ºC are estimated from gas geothermometers based on the fumarole gas compositions. The main origin of the water feeding the geothermal reservoir in Paka is meteoric as evidenced by stable isotope data.

1. Introduction

Paka geothermal prospect is characterized by a well-defined volcano and is one of the localities in the Kenya Rift endowed with geothermal resource potential. The Paka volcano is situated approximately 25 km north of Lake Baringo at 00° 25’N and 36° 12’E (Figure 1). The surface is rocky and rugged, covered by low cover of bush and shrubs. Widespread fumarolic activity, hot grounds and hydrothermally altered rocks characterize the geothermal prospect, particularly within the summit craters and to the northern flanks, with fine acicular crystals of sulfur depositions observed on the surface at a number of the fumarole sites. Lavas altered to red, purple and white clays, composed predominantly of kaolinite with alunite as described by Kemp (1990) were also common within the sites of active fumarolic activity.

Previous geochemical work in the prospect was carried by British Geological Survey (BGS) between 1988 and 1992 in an exploration survey of the northern sector of the Kenya Rift Valley (Dunkely et al., 1993). Their main objective was to investigate the geothermal activity of the volcanic centres between Lake Baringo and Lake Turkana. The results for Paka fumaroles from their survey indicated subsurface temperatures exceeding 300°C. Kenya Electricity Generating Company (KenGen) also conducted

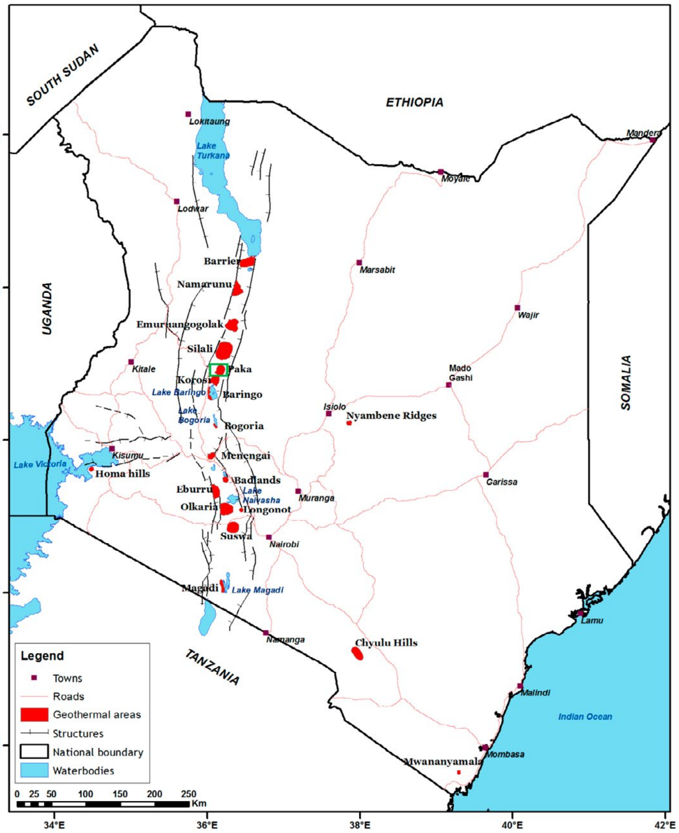

Figure 1. Map of Kenya showing the location of Paka geothermal prospect within the Kenya rift (highlighted with a green rectangle) and other central volcanoes (GDC, 2013).

geo-scientific work in the area in 2006/2007 (Lagat et al., 2007) with an aim of determining the existence of a geothermal system in Paka and developing a conceptual model of the system. The fumaroles sampled during the investigation however, were significantly contaminated hence the gas compositions reported indicate excessive subsurface condensation of steam.

This paper presents results of a geochemical survey carried out by Geothermal Development Company (GDC) in 2011. The main objective of the survey was to determine the chemical characteristics of the geothermal system in Paka using fumarole gas compositions as well as estimate prevailing reservoir temperatures. The fumaroles selected for sampling in 2011 were those with strong flows and recorded the highest outlet temperatures (at or close to the local boiling point). Hydrogen and oxygen stable isotope data from Clarke et al. (1990) and Dunkley et al. (1993) were used to infer the origin of the water recharging Paka geothermal system.

2. Geological Setting

Paka volcano lies in the inner trough of the Kenya Rift with the volcano massif extending over an area of about 280 km^2 and rises between 600-700 m above the rift floor. The Paka central volcano rises to a height of 1697 masl and is surrounded by plains to the north, south, west and east. At the summit is a well preserved caldera of about 1.5 km in diameter, which is filled with young basaltic flows. Several craters dotting the massif are aligned in a NNE direction. The volcano is cut on its central and eastern flanks by a swarm of NNE trending faults (see Figures 2 and 3).

The geology of Paka has been studied for various purposes, both for student research (e.g. Sceal, 1974) and surveys focusing on geothermal energy (e.g. Dunkley et al., 1993; Lagat et al., 2007 and Kanda et al., 2011). Paka is a small shield volcano constructed largely by trachyte and basaltic lavas and pyroclastic deposits. Much of the shields forming lavas are covered by trachytic pyroclastic deposits which are seen to cover the areas around the volcano. Basalt, hawaiite and mugearite lavas were erupted from a series of fissure and fault zones located on the lower northeastern and southern flanks. Volcanic activity commenced by 390 ka and continued to within 10 ka. Broadly contemporaneous trachytic and basaltic activity occurred on a number of small satellite centres peripheral to the main volcanic edifice. The oldest exposed rocks are the Lower Trachytes, which constructed an early volcanic shield. Subsequent fracturing of the shield by the NNE-trending faults was accompanied by eruption of the Lower Basalts from fissure sources on the eastern flanks of the volcano (Figure 2).

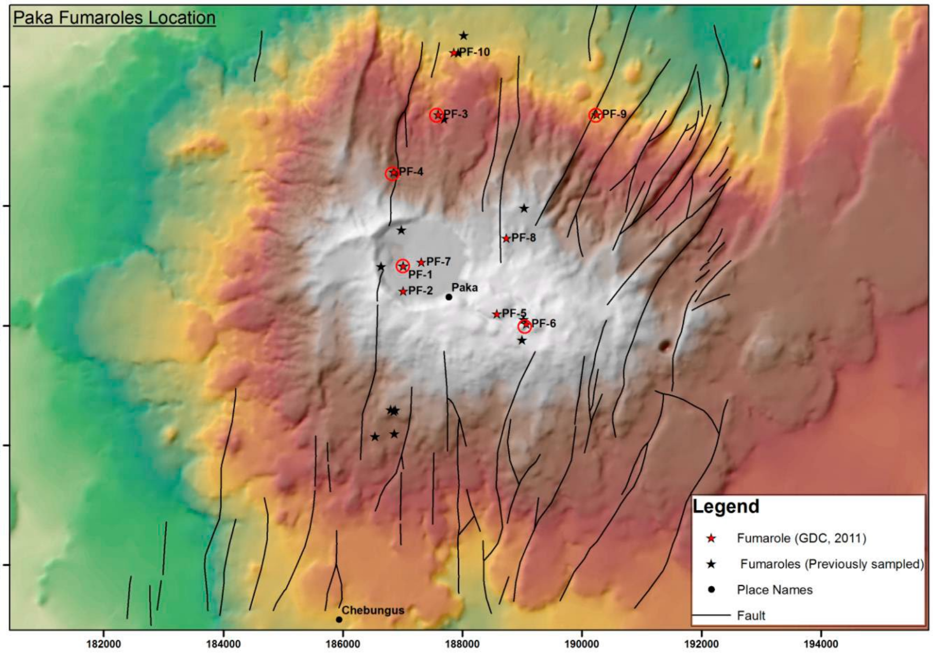

Figure 3. Location of sampled fumaroles (GDC, 2011) and those sampled during previous works. The fumaroles highlighted in circles are those that indicated little or no contamination.

3. Sampling and Analysis of Fumarole Discharges

Figure 3 shows the distribution of the fumaroles sampled in 2011. The discharge temperatures of the fumaroles ranged from

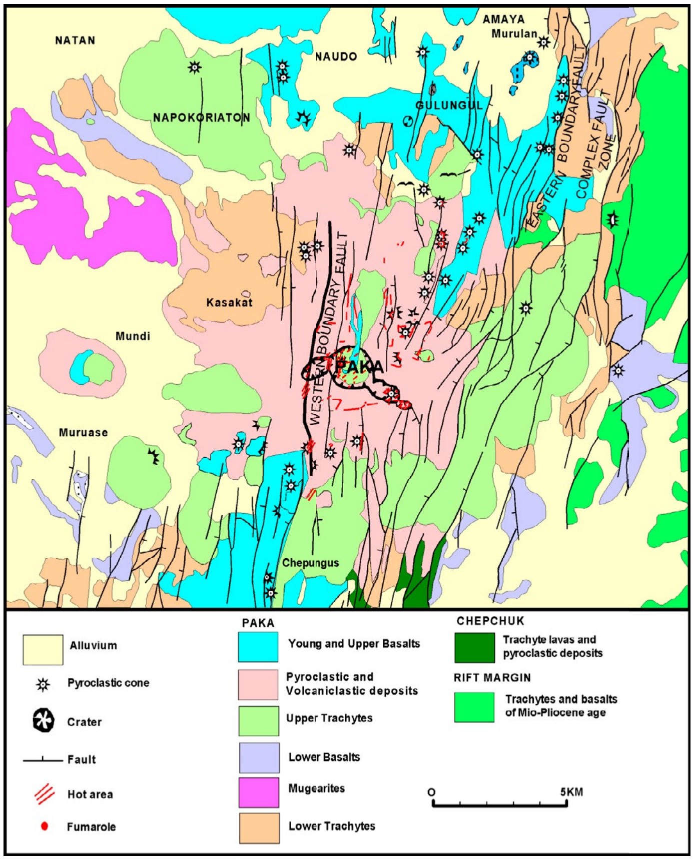

Figure 2. Geological map of Paka volcano and surrounding (Dunkley et al., 1993).

80°C to 95.7°C with about half of those sampled discharging at the local boiling point at the respective elevations.

The steam discharge from the fumaroles was trapped using a polypropylene funnel whose contact points with the ground were sealed with mud to prevent any contact with atmospheric air in order to avoid contamination of the discharge. The fumarole gases were then sampled by directing the steam into two evacuated gas sampling flasks, one at a time, containing 50 ml of 40% w/v NaOH solution. The more soluble gases non-condensable gases, H_2S and CO_2 are absorbed into the solution giving room in the evacuated flask for the less soluble ones (H_2, CH_4 and N_2) common in geothermal fluids to concentrate to measureable levels. One flask was used for analysis of CO_2 and H_2S titrimetrically using standardized HCl and mercuric acetate while the second flask was equilibrated for analysis of H_2, CH_4, N_2 and O_2 using gas chromatograph.

4. Results and Discussion

Gas composition of five (5) of the ten (10) fumaroles sampled in 2011 are shown in Table 1. The samples selected are those that indicated little or no atmospheric contamination as indicated by the presence of detectable oxygen. The presence or absence of oxygen is largely considered a good indicator of valid sampling or possible contamination prior to collection since it is generally taken to originate from the atmosphere. The results from the selected samples have consequently been utilized in the interpretations presented in this paper. This is because high temperature discharging fluids with strong outflows usually give an accurate indication of the deep fluid composition in an area. Contaminated samples are however much diluted, oxidized and cooled hence lose much of their original chemical identity through near surface reactions.

Table 1. Fumarole gas compositions in mmoles/kg.

Fumarole	Discharge Temp. (°C)	CO_2	H_2S	H_2	CH_4	N_2	O_2
PF-1	94.3	723	0.23	21	24	1.6	0
PF-3	95.3	163	0.03	0.4	0	29.8	6.6
PF-4	94.8	151	0.02	3.0	0.7	1.6	0
PF-6	94	2234	0.03	18	54	0	0
PF-9	95.7	225	0.01	0.9	0.2	1.8	0

The results presented in Table 1 show that carbon dioxide is the most abundant gas in geothermal fluids in Paka accounting for about 94 to 99% of the non-condensable gases present. The possible source of this gas is significantly mantle-derived as indicated by Darling et al. (1995). Hydrogen concentrations vary, with the highest value being 21 mmoles/kg reported in PF-1. High hydrogen concentrations are often taken to indicate proximity to or strength of hydrothermal upflows. Significantly low values of H_2S are however observed in the discharge which could be the consequence of secondary processes. Sulfur species are easily affected by secondary processes, such as the formation of sulfides and elemental sulfur, and hydrolysis process of sulfur gases (Giggenbach, 1996 and Yang et al., 2003). H_2 and H_2S are removed from steam in the upflow relative to CO_2. CO_2 is considered relatively inert whereas H_2S and H_2 are easily oxidized especially when rising steam encounters downward percolating water. Ellis and Mahon (1967) observed that some hydrogen sulfide may be lost from steam rising in natural channels, and near surface reaction of steam with organic materials may also create additional methane, ammonia and CO_2 in steam from minor steam vents. Additionally, precipitations of sulphide bearing minerals are reactions likely to take place during ascent of the fluids. Reactions involving H_2 and H_2S in the upflow zone form another possible explanation for the considerable depletion of H_2S in the fumarole discharges. Generally, the observed low H_2S concentrations in the Paka geothermal prospect could also be largely due to the Kenya Rift Valley (KRV) being a low sulphur province (Darling et al., 1995).

Paka fumaroles indicate relatively high CH_4 concentrations, with the highest at 54 mmoles/kg in PF-6. Methane is typically present in very small amounts in volcanic gases and considered a product of secondary processes, e.g. hydrothermal and/or organic processes (Giggenbach 1989; Goff and Janik, 2000). Giggenbach (1996) observed that species with slower kinetic responses, such as CH_4, are largely generated within slow-moving hydrothermal systems associated with most active volcanic structures.

The observed CH_4 values in Paka are possibly a result of the action of hot fluids on organic compounds. Studies in the KRV indicate that hydrocarbon values favor a thermogenic origin from organic matter entering the geothermal system (Allen and Darling, 1992; Darling et al., 1995; Darling, 1998). No correlation was found between $\delta^{13}C$ values of CO_2 and CH_4 in the Northern Kenya Rift (Dunkley et al., 1993). Dunkley et al. (1993) concluded that CH_4 could neither be of biogenic origin nor could it likely be synthesized from CO_2 or H_2 at high temperatures due to the absence of alkene gases which are thought to be produced under such conditions.

The results also indicate that non-condensable gas (NCG) content is low in the area to the north of the caldera (less than 1% by weight for fumaroles PF-3, PF-4 and PF-9) and slightly higher in fumaroles SF-1 and SF-6 located in the main caldera and the eastern crater respectively. This observation is important due to the fact that natural steam from major fumaroles gives a good indication of the quality of steam produced later by wells (Ellis and Mahon, 1977).

5. Gas Geothermometers

Relative proportions of gas in geothermal fluids are a function of temperature and have therefore been used to deduce the temperature of the source fluids (Giggenbach, 1980; Giggenbach, 1980; D'Amore and Panichi, 1980; Nehring and D'Amore, 1984; Arnorsson and Gunnarsson, 1985). Gas geothermometry functions developed by Arnorsson and Gunnarsson (1985) were used to calculate reservoir equilibrium temperatures in Paka. The results are shown in Table 2.

Table 2. Gas geothermometers (°C).

Fumarole	T_{CO2}	T_{H2S}	T_{H2}	$T_{CO2/H2}$
PF-1	320	218	305	298
PF-3	278	181	269	267
PF-4	276	167	287	293
PF-6	353	177	303	282
PF-9	288	159	276	273

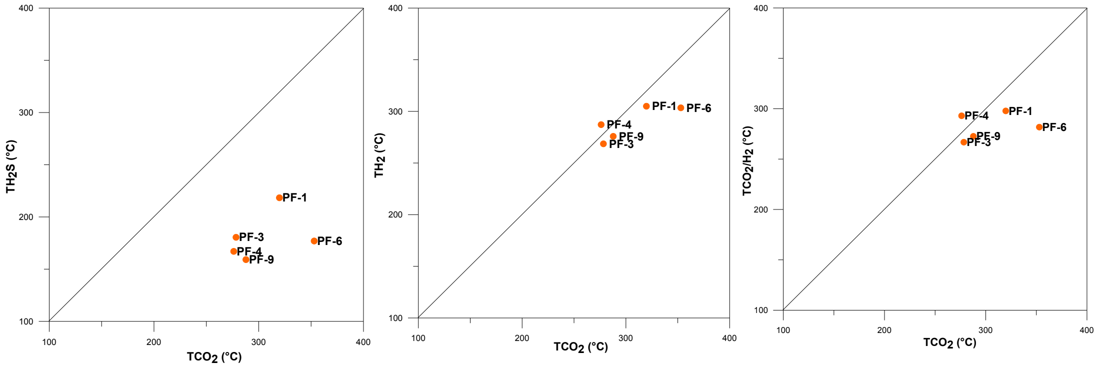

Figure 4. Relation between gas geothermometry in the Paka geothermal prospect.

Subsurface temperatures estimated using CO_2 and H_2 equilibrium functions are comparable except for PF-1 and PF-6 which give somewhat higher CO_2 equilibrium temperatures. The CO_2/H_2 ratio is assumed to yield conservative estimates since H_2 tends to be removed from the rising steam relative to CO_2, and may therefore be more reflective of the reservoir temperatures. The CO_2/H_2 ratio temperatures lie between 270°C and 300°C. The H_2S gas function however indicates lower temperature estimates which are unlikely to represent equilibrium conditions in the reservoir due to the factors discussed in the previous section. Figure 4 presents the relation between the gas geothermometry. There are similarities in CO_2, H_2 and CO_2/H_2 geothermometer temperatures as depicted by the somewhat linear relationship in the second and third graph in the figure indicating that steam condensation or phase segregation at elevated pressures/temperatures is insignificant for these fumaroles. This is particularly the case since strongest fumaroles are hot enough to prevent excessive condensation of water. The reason for the nonlinear relationship seen in the first graph is possibly the result of reactions involving H_2S and H_2 in the upflow.

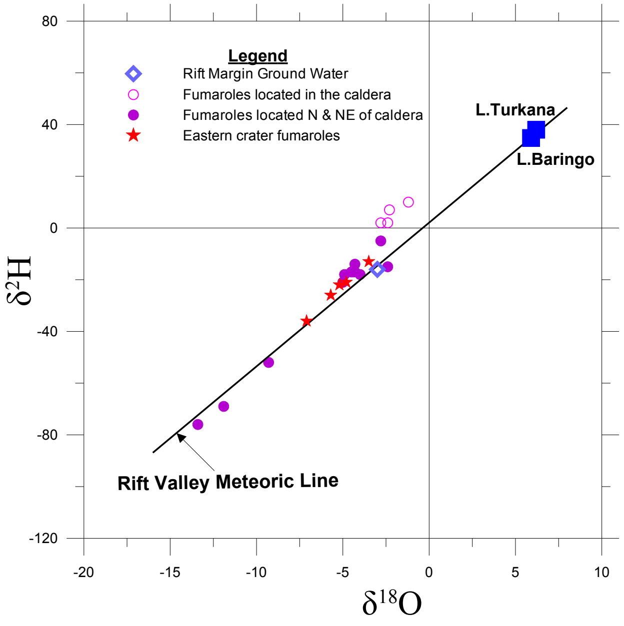

Figure 5. Plot of ď^{2}H against ď^{18}O for Paka fumaroles steam condensates (values in permil with respect to SMOW).

6. Isotope Data

Isotope results of the fumarole condensates in the Paka prospect used in this paper are those obtained by Dunkley et al. (1993). Hydrogen and oxygen stable isotope values calculated by Clarke et al. (1990) for lakes Baringo and Turkana are also used. The isotopic composition of the rift margin groundwater in this area has ď^{2}H and ď^{18}O of around -16‰ and -3‰ respectively.

Figure 5 shows isotopic variations in the fumarole discharges in Paka. The steam condensate samples are an elongate group parallel to the meteoric water line and covering a large range of approximately -1 to -13‰. There is no conspicuous ^{18}O shift except that the fumaroles located in the caldera are more enriched isotopically relative to those located in the eastern crater and to the north and north east of the caldera, some of which are much depleted. It is evident from the graph that the main source of the water feeding the geothermal reservoir in Paka is meteoric in origin i.e. rift margin ground water. Primary steam separation from the rift margin ground water is considered the major process that influences the observed isotopic compositions in the fumarole discharges. The isotope data for fumaroles located in the caldera however indicate the possibility that the water entering the reservoir may have already lost steam. Reflux condensation is the other possible mechanism that may have given rise to the isotopic variations as noted by Dunkley et al. (1993).

7. Conclusions

A high temperature geothermal system exists below the Paka volcano with reservoir temperatures in excess of 300°C as indicated by gas geothermometers. There is a good correlation between the CO_2 and H_2 equilibrium temperatures confirming the reliability of the estimated temperatures.

Carbon dioxide is the most abundant gas in the fumarole discharges in Paka (accounting for about 95% of the non-condensable gases). Significant H_2 concentrations are also noted indicating a high temperature source. Secondary processes and deposition of elemental sulfur are likely the main reasons for the reported low concentrations of H_2S in the fumarole discharges. The observed high CH_4 concentrations are likely thermogenic in origin, from organic matter entering the geothermal system.

The main origin of the water recharging the geothermal system in Paka is meteoric.

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