# Geochemical Study of Fumarolic Condensates from Paka Volcano, Kenya

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## ABSTRACT

Paka volcano is characterised by intense and widespread geothermal surface activity manifested in the form of fumaroles, hot grounds and hydrothermally altered rocks. It is located within the Kenya Rift Valley which is endowed with geothermal resource potential. This study seeks to reinterpret the results of a geochemical survey carried out by (Clarke, Woodhall, & Darling, 1990), (Dunkley, Smith, Allen, & Darling, 1993) and (Darling, Griesshaber, Andrews, Armannsson, & O'Nions, 1995). The main aims of this undertaking were to; (i) investigate the source of fluids in this volcano and their relationship with the tectonic assessment of the volcano; (ii) assess and evaluate the isotopic geothermometry temperatures; (iii) estimate the contributions of the three major $CO_2$ sources along convergent plate margins, i.e., the mantle, organic sediments, and marine limestones. The results of $^3He/^4He$ show that all the samples have values in excess of 1, indicating enrichment to varying degrees in mantle He, and the maximum ratio of 8.0 is comparable typical MORB values. The stable isotopes indicate that there is insufficient variation in the local groundwaters to account for all of the steam condensates by a simple process of primary steam separation from these waters. Fumarole 163 and 165 are more enriched in heavy isotopes than the local ambient groundwaters.

The $\delta^2H$ and $\delta^{18}O$ values of the steam condensate of most the samples are in reasonable agreement with the theoretical isotope compositions expected for the vapors separated through single-step boiling either at 250-100°C approximately from the undiluted deep geothermal liquid or at 310-250°C approximately from the diluted deep geothermal liquid. Isotopic geothermometry temperatures of samples 163 and 166 give 350 and 312°C, respectively, adopting the fractionation factors of Horita (2001), and 340 and 310°C, respectively, accepting the fractionation factors of Bottinga (1969). Despite all these the gases show a clear mantle origin.
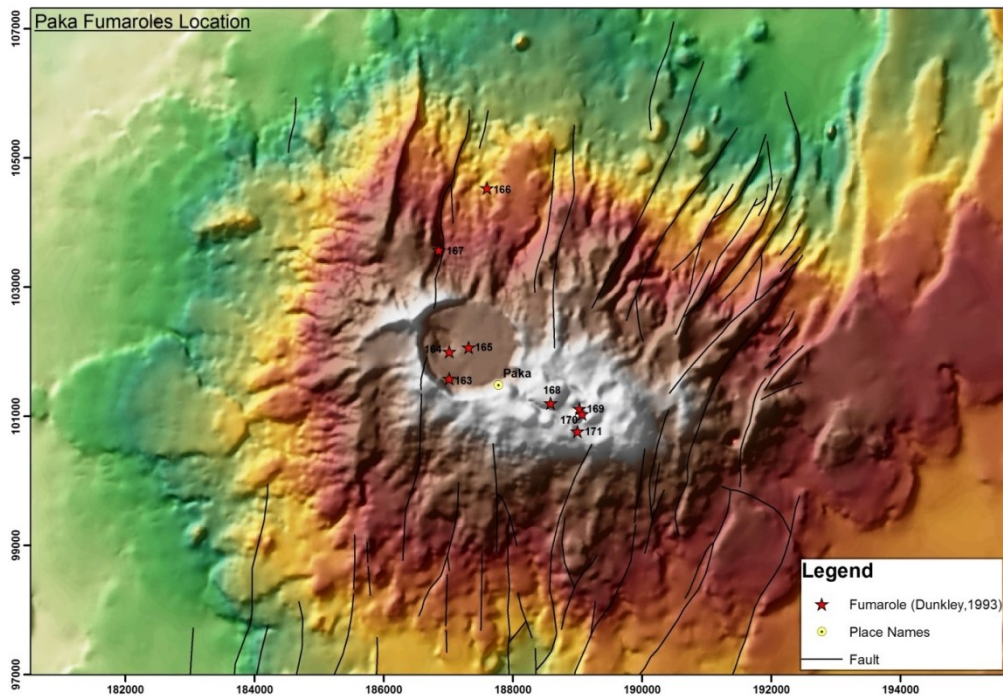
## 1. INTRODUCTION



Figure 1: Map showing the location of fumaroles in Paka volcano. Modified from (Dunkley, et al., 1993).

The Paka volcano is one of the localities in the Kenya Rift endowed with geothermal resource potential. Occurrence of a geothermal system at Paka is manifested by the widespread fumarolic activity, hot grounds and hydro thermally altered rocks. The Paka prospect is

located atop a very young volcano that is marked by recent (~10Ka) eruptions (Darling, et al., 1995; Dunkley, Smith, Allen, & Darling, 1994; Glover, 1972; Omenda, 2007; Sceal, 1974). Paka is a small shield volcano constructed largely by trachyte lavas and pyroclastic deposits. Surface geothermal activity is widely developed at Paka particularly within the summit craters and the northern flanks. It occurs in form of steaming grounds, fumaroles and hot grounds that is locally associated with intense hydrothermal alteration (Darling, et al., 1995). In some of these areas maximum temperatures exceed the local boiling point with the maximum temperature recorded being slightly over 97oC. Occurrences of Sulphur were observed in the fumaroles in the Eastern crater and it is an indication that the faults deep seated, and tapping directly from the magma.

The volcano is situated approximately 25 km north of Lake Baringo at 00° 25'N and 36° 12'E (Kipng'ok & Nyamongo, 2013) (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, 1989) were also common within the sites of active fumarolic activity (Kipng'ok & Nyamongo, 2013).

Previous work related to geochemistry was carried by British Geological Survey (BGS) between 1988 and 1992 in an exploration survey of the northern sector of the Kenya Rift Valley (Dunkley, et al., 1993). Their main objective was to investigate the geothermal activity of the volcanic centers 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 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 reinterprets the results of a geochemical survey carried out by (Clarke, et al., 1990), (Dunkley, et al., 1993) and (Darling, et al., 1995). The main aims of this undertaking were to; (i) investigate the source of fluids in this volcano and their relationship with the tectonic assessment of the volcano; (ii) assess and evaluate the isotopic geothermometry temperatures; (iii) estimate the contributions of the three major $CO_2$ sources along convergent plate margins, i.e., the mantle, organic sediments, and marine limestones. The fumaroles selected for this study include PK1a (163), Paka PK1b (164), PK1c (165), PK4a (166), Paka PK 4b (167), PK7a (168), Paka PK 7b (169), Paka PK 7c (170) and Paka PK 7d (171), as in Table1.

## 2. FUMAROLIC ISOTOPE GAS COMPOSITIONS

(Dunkley, et al., 1993) and (Darling, et al., 1995) reported the results of 3He/4He in the form of RA, which is the ratio of 3He/4He in the sample to that of the atmosphere (1.4 x 10-6) corrected for air contamination on the basis of the Ne/He ratio. The results showed that all the samples have values in excess of 1, indicating enrichment to varying degrees in mantle He, and the maximum ratio of 8.0 is comparable typical MORB values and with He issuing from the active carbonatites volcano of Oldoinyo Lengai in the rift in Northern Tanzania (Javoy, Pineau, Staudacher, Cheminee, & Krafft, 1989).

**Table 1: Fumarole condensate unstable isotope chemistry ($\delta^{13}$C in permil vs. PDB, He ratio in RA).**

| Fumarole | Code | Temp | $\delta^{13} C_{CO2}$ | $\delta^{13} C_{CH4}$ | $^3He/^4He$ | $C/^3He$ | Source |
|----------|------|------|------|------|------|------|--------|
| Paka PK1a | 163 | 96.2 | -2.9 | -24.9 | 7.9 | 2.4 | Darling et al., (1995) |
| Paka PK 4a | 166 | 95.3 | -3.4 | -27.8 | 6.17 | 3.2 | " |
| Paka PK 7a | 168 | 94 | -2.7 | -22.2 | 3.63 | 1.6 | " |

**Table 2: Fumarole condensate stable isotope chemistry in permil vs. SMOW.**

| Fumarole | Code | Temp | $\delta^2H$ | $\delta^{18}O$ | source |
|----------|------|------|------|------|--------|
| Paka PK1a | 163 | 96.2 | 7 | -2.3 | Dunkley et al.,(1993) |
| Paka PK1b | 164 | 91.2 | 10 | -1.2 | " |
| Paka PK1c | 165 | 91 | 2 | -2.8 | " |
| Paka PK 4b | 167 | 95.5 | -18 | -4 | " |
| Paka PK 7a | 168 | 94 | -13 | -3.5 | " |
| Paka PK 7b | 169 | 91 | -22 | -5.2 | " |
| Paka PK 7c | 170 | 91 | -21 | -4.8 | " |
| Paka PK 7d | 171 | 92 | -26 | -5.7 | " |

From the $\delta^{13}C$ values of approximately -20 to -30‰ (Dunkley, et al., 1993), it appears that the methane cannot be of biogenic origin, but neither is it likely to be synthesised from CO2 or H2 at high temperatures because of the absence of alkene gases which are thought to be produced under such conditions.

As for the stable isotopes, (Dunkley, et al., 1993) indicate that there is insufficient variation in the local groundwaters to account for all of the steam condensates by a simple process of primary steam separation from these waters. Fumarole 163 and 165 are more enriched in heavy isotopes than the local ambient groundwaters.

## 2.1 The $\delta^2H$ and $\delta^{18}O$ Values of Fumarolic Steam Condensates

Before investigating the isotope characteristics of fumarolic steam condensates from the study area, it is advisable to inspect the correlation plots of $\delta^2H$ values vs. temperature and $\delta^{18}O$ values vs. temperature (Figure 2). Both diagrams point out the occurrence of a significant correlation between isotope values and outlet temperature of fumarolic discharges, excluding samples 164, 165 and 167 which shows anomalously high $\delta^2H$ and $\delta^{18}O$ values. Excluding samples 164,165 and 167, the following linear regression equations between isotope values and outlet temperature (in °C) have been obtained.

$$\delta^2H = 5.0884 \cdot T - 517.9 \qquad (N = 4; R^2 = 0.9174) \qquad (1)$$

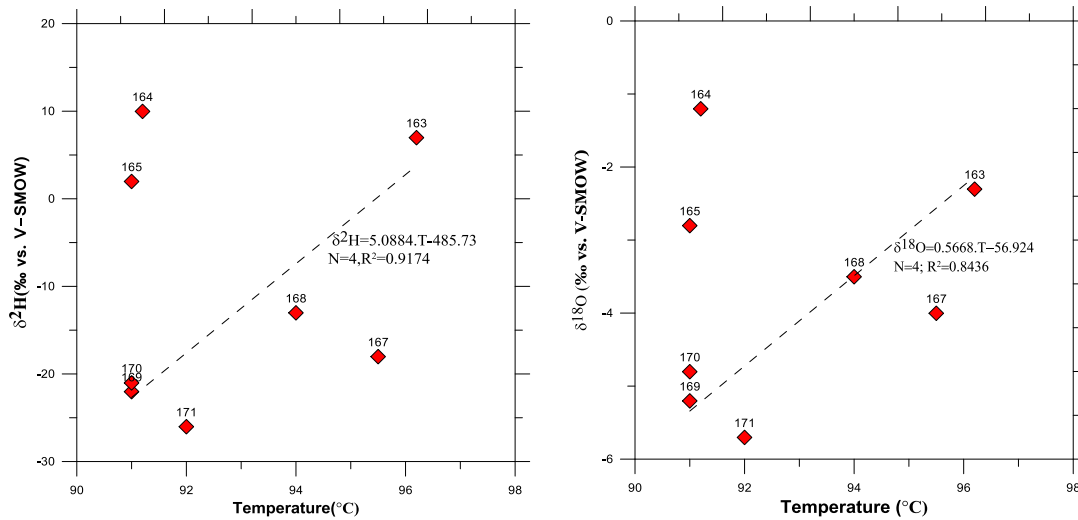$$\delta^{18}O = 0.5668 \cdot T - 55.99 \qquad (N = 4; R^2 = 0.8436) \qquad (2)$$



**Figure 2: Correlation plots of temperature vs. $\delta^2H$ values, left and temperature vs. $\delta^{18}O$ values, (right) values for the fumarolic steam condensates from Paka.**

Equations (1) and (2) have then been used to compute the $\delta^2H$ and $\delta^{18}O$ values of samples 164,165 and 167, which resulted to be -53.84‰ and -4.30‰, -54.86‰ and -4.41‰ and -31.96‰ and -1.86‰ respectively. These calculated isotope values differ from the measured values (10‰ and -1.2‰, 2‰ and -2.8‰ and -18‰ and -4‰, respectively) much more than expected based on analytical uncertainties (typically ±1‰ for $\delta^2H$ values and ±0.05‰ for $\delta^{18}O$ values) and have been adopted in the following discussion.

That the $\delta^2H$ and $\delta^{18}O$ values (both indicated as $\delta_V$) of the vapor separated at temperature $T_S$, in a single-step, from a geothermal liquid of incipient boiling temperature $T_O$ and isotopic composition $\delta_O$ are constrained by the following relation (Giggenbach, 1987; Giggenbach & Stewart, 1982), which is based on the assumption of isotopic equilibrium between separated vapor and liquid at separation temperature:

$$\delta_V = \delta_O - 1000 \ln\alpha_{L-V} (1 - y) \qquad (3)$$

In this equation, $1000 \ln\alpha_{L-V}$ is the liquid-vapor equilibrium fractionation factor at separation temperature and y is the steam fraction, which is computed by means of the following relationship for isoenthalpic steam separation:

$$y = \frac{H_O - H_L}{H_V - H_L} \qquad (4)$$

Where H stands for the specific enthalpy of the subscripted phase under saturation conditions, i.e., coexistence of vapor and liquid. Use of the enthalpies of pure water (Lemmon, McLinden, & Friend, 2005) is a reasonable approximation as long as the contents of dissolved substances in geothermal liquids are low enough.
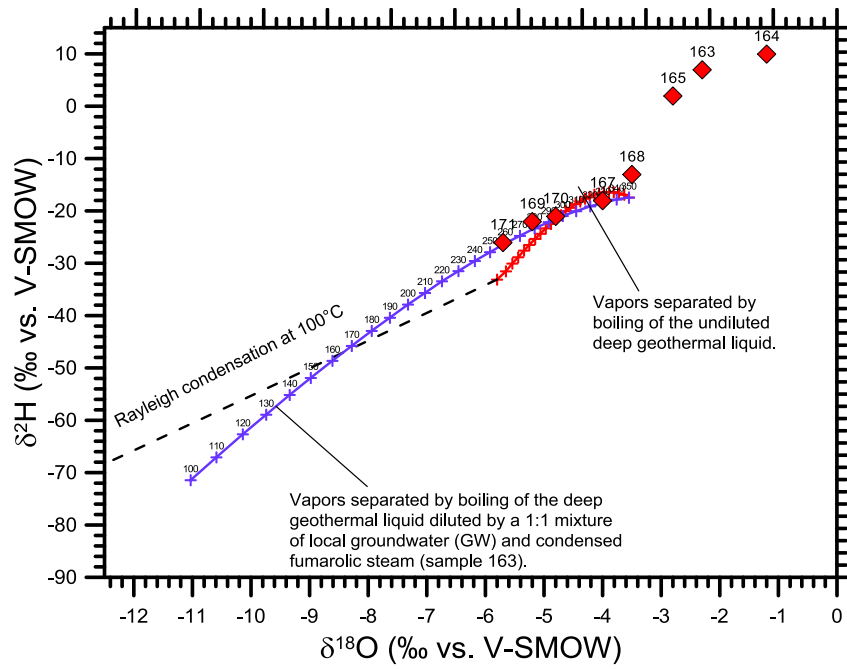
**Figure 3: Correlation plot of $\delta^2$H vs. $\delta^{18}$O values for the fumarolic steam condensates from the study area. Also shown are the theoretical isotope composition of the vapors separated at decreasing temperature (at steps of 10°C, until 100°C) through single-step boiling of both (i) the undiluted deep geothermal liquid, initially at 350°C (red line and crosses; separation temperatures are not indicated) and (ii) the deep geothermal liquid diluted through addition of a 1:1 mixture of local groundwater and fumarolic steam condensate, represented by sample 163 (violet line and crosses; separation temperatures are indicated). The theoretical isotope composition of the residual steam generated through Rayleigh condensation at 100°C from the vapor separated at 100°C through boiling of the undiluted deep geothermal liquid is also reported (black dashed line).**

Since separated vapor and liquid are assumed to be in isotopic equilibrium at separation temperature, the isotopic composition of the separated liquid is then computed by means of the equation:

$$\delta_L = \delta_V + 1000 \ln\alpha_{L\text{-}V} \tag{5}$$

Liquid-vapor fractionation factors of O and H isotopes for pure water from 0°C to the critical temperature are given by the following relationships ((Horita & Wesolowski, 1994), T in K):

$$1000 \cdot \ln\alpha_{L-V(^2H)} = 1158.8 \frac{T^3}{10^9} - 1620.1 \frac{T^2}{10^6} + 794.84 \frac{T}{10^3} - 161.04 + 2.9992 \frac{10^9}{T^3} \tag{6}$$

$$1000 \cdot \ln\alpha_{L-V(^{18}O)} = -7.685 + 6.7123 \frac{10^3}{T} - 1.6664 \frac{10^6}{T^2} + 0.35041 \frac{10^9}{T^3} \tag{7}$$

Another process possibly affecting vapor discharges is Rayleigh condensation at 100°C or a slightly lower temperature. The isotopic effects of this process were computed by means of the following relationship (e.g., (Faure, 1986); (Clark & Fritz, 1997)):

$$\delta_V = \left(\delta_{V,O} + 1000\right) \cdot \left(1 - c\right)^{(\alpha_{L-V} - 1)} - 1000 \tag{8}$$

Where $\delta_{V,O}$ and $\delta_V$ refer to the isotopic composition of the steam before condensation and after condensation, respectively, and c is the fraction of condensed steam.

By using equations (3) to (5) and the fractionation factors given by equations (6) and (7), the $\delta^2$H and $\delta^{18}$O values were computed for the vapors separated in a single step at decreasing temperatures $T_S$ (at intervals of 10°C, until 100°C) from a boiling geothermal liquid with the average isotope composition of sample 163 (namely $\delta^2$H = -7 ‰ and $\delta^{18}$O = -2.3 ‰) and an initial temperature $T_O$ of 350°C. The choice of this temperature is based on the gas geothermometry. Results are represented by the red line and crosses in Figure 3.

The $\delta^2H$ and $\delta^{18}O$ values were also calculated for the vapors separated in a single step at decreasing temperatures $T_S$ (at intervals of 10°C, until 100°C) from the deep geothermal liquid diluted through addition of a 1:1 mixture of local groundwater and fumarolic steam condensate, represented by sample 163 (T = 96.3°C). Owing to the lack of analytical data, the isotope composition of local groundwater was computed by means of equations (9) and (10) for an infiltration altitude of 1250 m asl, which is reasonable assumption for the upper parts of the Paka volcano all around the caldera, obtaining a $\delta^2H$ value of -7.7‰ and a $\delta^{18}O$ value of -1.64‰.

$$\delta^{18}O = -0.0029\,H + 1.99 \tag{9}$$

$$\delta^2H = -0.0148\,H + 10.82 \tag{10}$$

The temperature of local groundwater was assumed to be 34.5°C based on the ambient borehole temperature of the area. Results are represented by the violet line and crosses in Figure 3.

The effects of Rayleigh condensation at 100°C on the vapor separated at 100°C through boiling of the undiluted deep geothermal liquid have been computed too. Results are shown by the black dashed line in Figure 3.

The $\delta^2H$ and $\delta^{18}O$ values of the steam condensate samples 166, 167, 168,169,170 and 171 are in reasonable agreement with the theoretical isotope compositions expected for the vapors separated through single-step boiling either: (i) at 250-100°C approximately from the undiluted deep geothermal liquid or (ii) at 310-250°C approximately from the diluted deep geothermal liquid. Samples 163,164 and 165 can be explained assuming either single-step separation at 100°C from the undiluted deep geothermal liquid followed by limited steam condensation or single-step separation at 190-220°C from the diluted deep geothermal liquid.

The isotope values of these three fumaroles, all positioned in the central caldera (see Figure 1 for the location of fumaroles and steaming grounds), suggest that they represent the surface expression of the major upflow zone of the deep reservoir liquid.

The isotope compositions of steam condensate samples 168,169,170 and 171 (collected in the eastern caldera) can be explained assuming either single-step separation at 100°C from the undiluted deep geothermal liquid followed by considerable steam condensation or single-step separation at 150-210°C from the diluted deep geothermal liquid. These sites correspond to peripheral locations with respect to the major upflow zone of the deep reservoir liquid.

Finally, the steam condensate samples 167 and 168, collected outside the caldera, to the north, exhibits a very light isotope composition, in reasonable agreement with the theoretical $\delta^2H$ and $\delta^{18}O$ values expected for the vapor separated through single-step boiling at 100°C approximately from the diluted deep geothermal liquid. Also this site corresponds to a marginal position with respect to the major upflow zone of the deep reservoir liquid.
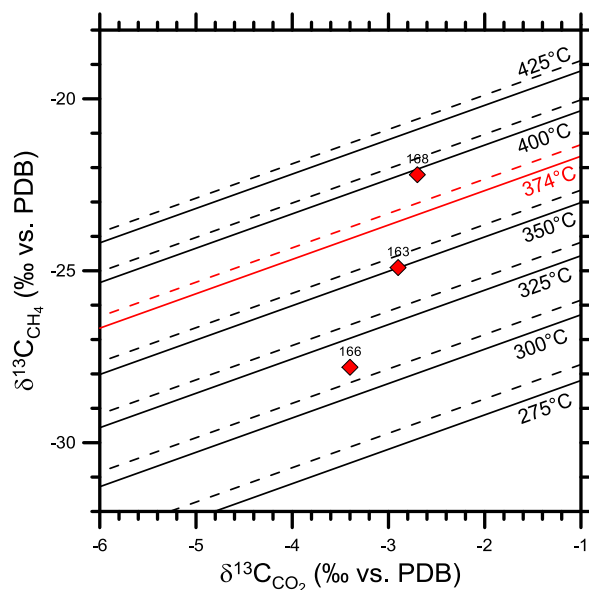
## 2.2 The $\delta^{13}C$ of Carbon Dioxide and Methane



**Figure 4: Plot of $\delta^{13}C_{CH4}$ vs. $\delta^{13}C_{CO2}$ values for the gases of the study area, also showing the isotherms computed by means of the equilibrium isotope fractionation factors of both (Bottinga, 1969), dashed lines, and (Horita, 2001), solid lines.**

The $\delta^{13}C$ values of $CO_2$ and $CH_4$ have been measured for some fumarolic effluents from Paka volcano (Table 2) ((Dunkley, et al., 1993); (Darling, et al., 1995)). Samples analysed for the $\delta^{13}C$ values of both $CO_2$ and $CH_4$ are represented in the plot of $\delta^{13}C_{CH4}$ vs.

$\delta^{13}C_{CO2}$ (Figure 4), also showing relevant isotherms computed by means of the equilibrium isotope fractionation factors of both (Bottinga, 1969) and (Horita, 2001), which differ by 0.30 to 0.45‰ units at temperatures between 430 and 280°C.

According to the data samples 163,166 and 168 have almost similar $\delta^{13}C$ values of $CO_2$, ranging from -2.9 to -3.4‰. Sample 168 gave the lowest values probably due to absorption of atmospheric $CO_2$ during sample storage. This is a recurrent problem when isotopic $CO_2$ analyses are performed on Giggenbach's bottles, whereas this problem is not reported when isotopic measurements of $CO_2$ are undertaken on dry gas samples (Marini & Fiebig, 2005). While the $\delta^{13}C$ values of $CH_4$ are inversely related with temperature and $H_2O$ concentrations. According to the results sample 168 (-22.2‰) appears to most affected by secondary processes whereas samples 163 and 166 (-24.9 ‰and -27.8‰) are the least affected.

Based on this analysis data of available data, the most reliable geothermometric indications are provided by samples 163 and 166, that is: (i) 350 and 312°C, respectively, adopting the fractionation factors of (Horita, 2001), and (ii) 340 and 310°C, respectively, accepting the fractionation factors of (Bottinga, 1969).

## 2.3 The $CO_2/^3He$ Ratios

The $CO_2/^3He$ ratios reported by (Darling, et al., 1995), see Table 1, are contrasted with the corresponding $\delta^{13}C$ values of $CO_2$ in the plot of Figure 5 ( from Sano & Marty, 1995). This effective graphical tool was originally proposed to estimate the contributions of the three major $CO_2$ sources along convergent plate margins, i.e., the mantle, organic sediments, and marine limestones. Interestingly, Paka fumarolic gases have typical mantle values, as already noted by (Darling, et al., 1995).
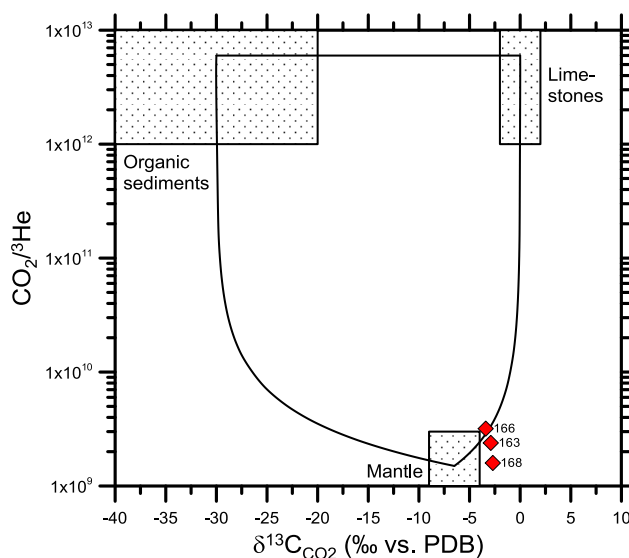


**Figure 5: Plot of $\delta^{13}C_{CO2}$ values vs. $CO_2/^3He$ ratio ( from Sano & Marty, 1995), showing the characteristics of the three main $CO_2$ sources (mantle, organic sediments, and limestones) and their contribution to the fumarolic fluids of Paka.**

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