# Application of Gas Geochemistry to Characterize Reservoir fluid in the Olkaria Domes Geothermal Field, Kenya

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Keywords: Gas, mineral equilibria, aquifer, partial pressure, Olkaria

#### **ABSTRACT**

The chemical composition of geothermal fluids provides critical information about the nature, geology, chemistry and hydrology of that geothermal system. One of the major chemical constituents that is applied in the understanding of the geothermal system is the concentration of the gases in steam. Geothermal discharges from wells have in their vapour phase some amount of gases including CO<sub>2</sub>, H<sub>2</sub>S, CH<sub>4</sub>, N<sub>2</sub>, H<sub>2</sub> and NH<sub>3</sub>. The partial pressure of gases like CO<sub>2</sub> are controlled or related to the aquifer temperature. The partial pressure of H<sub>2</sub> and H<sub>2</sub>S are fixed by temperature dependent mineral equilibria. The mineral buffer Clinozoisite-prehnite-quartz-calcite could control the aquifer partial pressure of CO<sub>2</sub> while H<sub>2</sub> and H<sub>2</sub>S are buffered by the mineral assemblage pyrite-pyrrhotite-magnetite. The partial pressure of CO<sub>2</sub> is in equilibrium with the mineral buffer Clinozoisite+ quartz+ calcite+ prehnite for the wells OW 916 and OW 904 A while OW 905A and OW 910 are tenths of magnitude far away. The partial pressure of H<sub>2</sub>S for OW 916 is in equilibrium with the mineral buffer Pyr + Pyrr + Mag, while OW 904, OW 904A are slightly off. However, they are all off the mineral buffer Pyr + Pyrr + Fre + Epi, which clearly is not contributing to the concentration of these gases. The partial pressure of H<sub>2</sub> has similar representation as that for H<sub>2</sub>S only that in this case, the data for OW 905A is slightly off the equilibrium line unlike in the H<sub>2</sub>S plot where it was on the line. NCG content of selected wells in the Olkaria domes wells over a period of time gives two different clusters. The first cluster is represented by OW 910 and OW 916. This represents wells in the eastern side of the domes area. These are characterised by lower NCG contents of averagely 0.5 – 0.6 %. The other wells OW 905A, OW 904 and OW 904A are characterised by higher NCG contents of > 1% up to 1.8%.

### 1. INTRODUCTION

Several parameters are often measured and analysed in trying to understand the nature of a geothermal system. These include the temperature, pressure and chemistry of the system in question. Geothermal fluids normally rise to the surface in the form of hot water and steam that have abundance of dissolved solutes and gases. The chemical composition of these fluids provides critical information about the nature, Geology, chemistry and hydrology of that geothermal system. This is an important aspect in the management of the geothermal resource (Arnórsson, et, al. 2006). One of the major chemical constituent that is applied in the understanding of the geothermal system is the concentration of the gases in steam. Geothermal discharges from wells have in their vapour phase some amount of gases including CO<sub>2</sub>, H<sub>2</sub>S, CH<sub>4</sub>, N<sub>2</sub>, H<sub>2</sub> and NH<sub>3</sub>. Carbon dioxide and H<sub>2</sub>S have the highest percentage by weight of all the gases in the vapour phase. As the gases partition from the liquid phase on the onset of boiling, the degree of their solubility will determine the percentage that actually fractionates. The more soluble gases H<sub>2</sub>S and CO<sub>2</sub> are therefore bound to be found in both the liquid and vapour phase. As the steam flows from source towards the surface, there occurs changes in the gas chemistry based on the temperature and the solubility of the gases (Nicholson, 1993). This could then be used to characterize the processes or type of fluid occurring within a particular well .The partial pressure of gases like CO2 are controlled or related to the aquifer temperature as noted by Arnórsson, (1985). They also show that the partial pressure of H<sub>2</sub> and H<sub>2</sub>S are fixed by temperature dependent mineral equilibria. Stefansson and Arnórsson, (2002) have shown that the partial pressure of specific gases are controlled mineral dependent equilibria. From their analysis, the aquifer partial pressure of CO2 could be controlled by the mineral buffer Clinozoisite-prehnite-quartz-calcite at temperatures above 220°C. H<sub>2</sub> and H<sub>2</sub>S were seen to be buffered by the mineral assemblage pyrite-pyrrhotite-magnetite. From this, it is evident that the relationship between the partial pressure and mineral assemblages could be used to characterize the nature of the reservoir fluid.

## 2. STUDY AREA

The Olkaria geothermal project is located approximately 120 Km NW of Nairobi, on the floor of the southern segment of Kenya's Rift valley. The Olkaria concession covers an area of 204 Km². About 14 prospects have been identified in the Kenyan Rift valley as having a potential for geothermal development. Of these, geothermal exploration has been done in almost all these areas, but currently development is limited to Olkaria, Eburru and Menengai Geothermal fields. Currently, close to 300 wells have been drilled in Olkaria both vertical and directional wells including reinjection, monitoring and production wells. The Olkaria geothermal field is divided into seven sectors; Olkaria E, Olkaria NE, Olkaria C, Olkaria SW, Olkaria NW and Olkaria SE. Production from geothermal resources started in 1981 with the construction of the Olkaria I power plant that currently has a production capacity of 45 MW. An additional 140 MW Olkaria IAU power plant was commissioned in 2014, in this part of the field. In the Olkaria NE, the Olkaria II power plant exists with a production capacity of 105 MW. The Olkaria IV power plant with a capacity of 140 Mw was commissioned in 2014 in the Olkaria domes area, site for the soon to be commissioned 165Mw Olkaria V power plant. The project also has a number of wellhead generators contributing approximately 70 Mw to the grid. The Olkaria geothermal field has varied chemistry in the different sectors within it. The water discharged from wells in the Olkaria field is low in dissolved solids compared to water from most other drilled high-temperature geothermal fields in the world with Chloride concentrations in water at the weir box ranging between 50 and 1100 ppm. The water from wells in Olkaria East and Northeast are the highest in chloride. The high chloride could be because of up flow of deep high-temperature geothermal fluid, although progressive boiling by heat flow from the rock may also

be a contributing factor as in the Olkaria East field. The chloride, sulphate and bicarbonate ternary plots show that wells in the Olkaria East production field and in Olkaria Northeast discharge sodium-chloride type water while the Olkaria West has the bicarbonate type. Wells in the Olkaria Central and Domes fields discharge a mixture of chloride and bicarbonate water. Temperature and pressure distribution across the entire field have been studied and indicate that fluid movement in the Olkaria geothermal area is associated with tectonic structures. The Olkaria East reservoir is two-phase, at least to the depth penetrated by the deepest wells.

## 2.1 Olkaria Domes Area

As discussed above, the Olkaria Domes is one of the sectors of the Greater Olkaria Geothermal area, located on the Southeastern edge of the prospect. This is the location for this study. Geo-scientific studies in the Domes area were carried out between 1992 and 1997. Exploration drilling took place in 1998 and 1999 where three wells (OW-901, OW-902, and OW-903) were drilled. All the three wells were successful and able to discharge. Further geophysical work coupled with a review of data from the three wells resulted in the siting of six appraisal wells in 2007. These were deviated wells and were drilled to a depth of between 2800 m to 3000 m. All of the six wells showed good results with some of them encountering temperatures as high as over 300°C. The data from these wells aided in the siting of production wells. At the end of 2018, close to 70 wells had been drilled in the Domes field. Data from these wells has proved the presence of enough steam to support the 140 MWe Olkaria IV plant and the soon to be commissioned 165 MWe Olkaria V 180 power plant. For this study, data from OW 914, OW 916, OW 904A and OW 903A will be used.

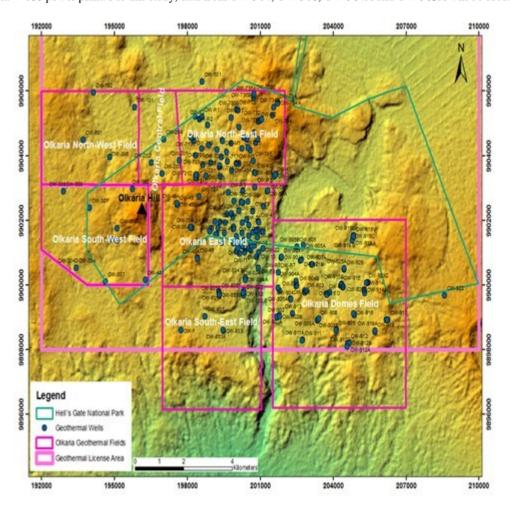


Figure 1: The sub-fields of Olkaria geothermal field (modified from Otieno 2016).

## 2.2 Geology

The Olkaria volcanic complex is part of the volcanic centres in the Central Kenya Rift associated with quaternary silicic volcanism. The Olkaria geology has been divided into five broad litho-stratigraphic groups based on age stratigraphy and lithology. These include the Mau tuffs, Plateau trachytes, Olkaria basalts and upper Olkaria volcanics. The rocks occurring on the surface in Olkaria geothermal area include rhyolite flows and pyroclastic deposits. Plateau trachytes is the reservoir rock for the East, Northeast, Southeast and Domes fields. Its thickness has been estimated to be greater than 1.5 km based on borehole data from these fields e.g., Mwangi, (2012) and Okoo, (2013). The structural domains of Olkaria are dominated by NE-SW and NW-SE striking faults, and subordinate N-S, NNE-SSW and ENE-WSW structural trending patterns. The presence of faults on the surface in the Domes area is severely limited by the substantial blanketing of the surface geology by thick, younger pyroclastic deposits (Otieno et al., 2014).

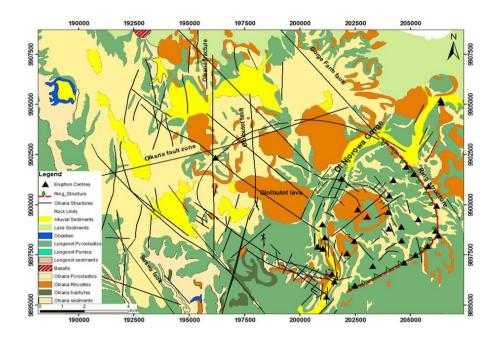


Figure 2: The Geology of Olkaria from Otieno, (2016), modified from Clarke, et. al. (1990).

#### 3. METHODOLOGY

#### 3.1 Sampling and analysis

Sampling and collection of fluids for chemical analysis was based on the procedures described by Arnórsson et al., (2007) for high temperature wells. These wells discharge a two phase fluid and sampling and collection of samples was done on the two phase line. The liquid and steam samples were collected using a webre separator. Fluid is allowed to flow into the separator by opening the vents. The valves in the separator are adjusted so that the pressure in the webre separator is close to that in the well head. The sampling pressure and temperature is recorded. For the liquid sample the needle valve and the ball valve of the webre separator were completely opened to release steam and ensure that only liquid is sampled from the water port (no bubbles) and collected into different bottles. The analysis was done according to standard methods for geothermal fluid analysis as described by Armansson and Ólafsson, (2000).

## 3.2 Data handling

Chemistry data of the wells since production begun was used to calculate the reservoir composition. The WATCH program version 2.4 (Bjarnason, 2010) was used to calculate the aquifer fluid composition from the data on the well discharge composition and taking into account the effect of excess enthalpy. This was based on the established reservoir temperatures at the depth of the major aquifers obtained from temperature logs. The sampling pressure was also incorporated as well as the discharge enthalpies of the respective wells. The non-condensable gas concentration in terms of the weight percentage was considered based on the average total mass of CO<sub>2</sub>, H<sub>2</sub>S, H<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub>. The NCG was calculated to the pressure of interest (separation pressure) from the sampling pressure. This was to correct for the varying gas sampling pressures with the webre separator.

The mineral saturation state is calculated based on,

$$SI = \log(Q/K) \tag{1}$$

Where K is the equilibrium solubility constant and Q is the activity product (Q) given by,

$$Q = \prod_i a_i^{v_i} \tag{2}$$

And  $a_i$  are the respective aqueous species activities raised to the power of its stoichiometric coefficient  $v_i$ , which is negative for reactants and positive for products,  $\prod I$  is the sum. Here the aqueous speciation was calculated using the WATCH 2.4 program (Arnórsson et al., 1982; Bjarnason, 2010). The solubility constants for the pure minerals and mineral buffer reactions were taken from Karingithi et al. (2010). The logarithms of CO<sub>2</sub> partial pressures were computed using the WATCH programme based on methods described by Stefánsson and Arnórsson (2002). The aquifer temperatures were calculated based on the reservoir fluid composition for three geothermometers, quartz ( $t_{qtz}$ ), Na/K ( $t_{Na/K}$ ) and H<sub>2</sub>S ( $t_{H2S}$ ), and those compared to the measured down-hole temperatures of the producing aquifers.

## 4. RESULTS AND DISCUSSIONS

The process of fluid-rock interaction results in the dissolution of the rock and its primary minerals and the formation of alteration minerals. In consideration of fluid-rock interaction, we assume that there is a localised equilibrium between the minerals and solution. The secondary minerals in active geothermal systems usually adopt certain depth and zonal distribution based on the temperature and pressure conditions in the reservoir. To be able to understand how certain minerals are controlling the gas equilibria in the system, the alteration mineralogy within that system has to be analysed to know the exact characteristics of those minerals within the reservoir.

Lagat (2004) discussed the hydrothermal minerals that are found within the Olkaria geothermal system. Adularia, albite, biotite, calcite, chlorite, pyrite, epidote, Fe-oxides, fluorite, garnet and illite are the major minerals. There is also occurrences of andradite, grossular, calcite, clinozoisite, epidote, fluorite, magnetite, prehnite, pyrite, pyrrhotite and wollastonite depending on the temperatures of the different wells where the samples were taken from. Figure 3 and 4 below show the mineralogical zonation in some wells in the domes area.

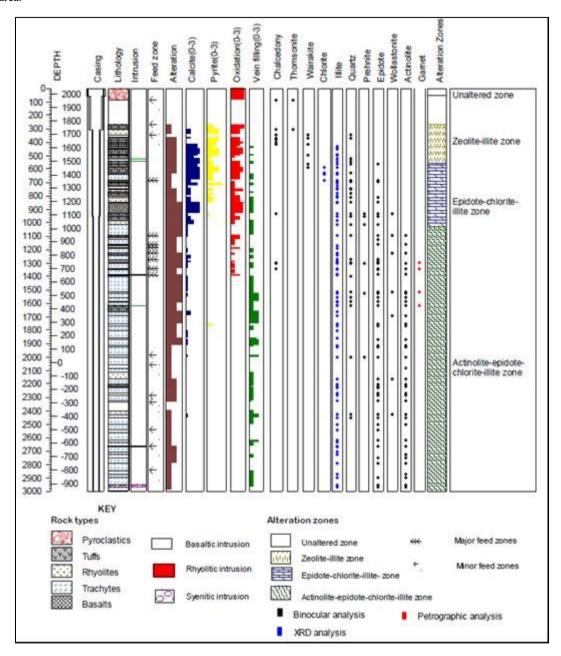


Figure 3: Lithology, alteration minerals and alteration zones of OW-916 (from KenGen internal report)

From this figure, it is evident that zones indicative of high temperatures, e.g. illite-chlorite-epidote and chlorite-epidote-actinolite, marked by the first appearence of epidote and actinolite, respectively are present at relatively shallow depths between 1280-1440 masl in OW 916 which is similar to that in OW-914. This generally charecterises most of the wells in this eastern zone of the domes. Looking at figure 4 below, the same zones appear at relatively greater depths in well OW-905A, and is also a longer zone, which similarly charecterises other wells aaroung the central western sector of the domes. Considering this fact, from a geologic perspective, there seems to be a distinction between the aquifers or reservoir charectristics in this particular wells/zones. Thus, looking at the gas chemistry from this wells, then a distinction can be made to collaborate what the mineralogy shows. Concentrations of reactive gases are be controlled by equilibrium with respect to specific mineral assemblage. Various mineral assemblage have been expressed that can control this reactions and this can be related to the mineralogical zones that are seen in these logs. As discussed by Stefansson and Arnórsson, (2002), certain mineral buffers control the concentration and occurrence of reactive gases in the geothermal system. If the calculated gas partial pressures of CO<sub>2</sub>, H<sub>2</sub>S,H<sub>2</sub> and CH<sub>4</sub> in the aquifer fluids are plotted against the equations of reaction and equilibrium constants of these mineral buffers, then a clear distinction can be made for each specific well. They showed that aquifer partial pressures of CO<sub>2</sub> matched well the equilibrium pressures of the mineral buffer clinozoisite–prehnite–quartz– calcite at temperatures above 220°C. The equation clinozoisite-calcite-quartz-grossular has also been considered for CO<sub>2</sub>. The mineral buffer pyrite-pyrrhotite- prehnite-epidote and pyrrhotite-pyrite-magnetite are thought to buffer H<sub>2</sub>S and H<sub>2</sub> partial pressures in

geothermal fluids and are considered for the domes wells. The temperature equations of the gases used are those from Karingithi et. al., (2010)

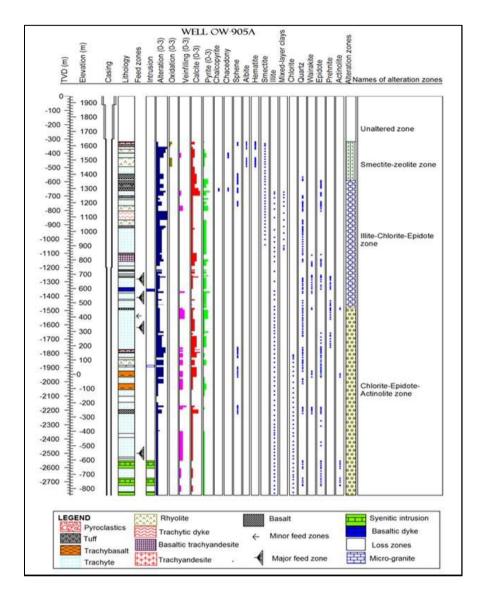


Figure 4: Lithology, alteration minerals and alteration zones of OW-905A (from KenGen Internal report)

The calculated partial pressures of CO<sub>2</sub>, H<sub>2</sub>S and H<sub>2</sub> from the selected wells was plotted against the aquifer temperature and considering the minerals in equilibrium with geothermal fluid. From Karingithi et. al., (2010), and Wanyonyi, (2014), it has been shown that there is equilibrium between geothermal fluid and minerals like Epidote, Calcite, quartz and prehnite. Figure 5 below shows the plot of the calculated partial pressure in the aquifers with the continuous line representing the mineral buffers of interest. Table 1 below shows the temperature constants used.

Table 1: Temperature equations for the equilibrium constants for mineral pairs that control gas concentrations in solution. The equations are valid in the range  $0-350^{\circ}$ C at  $P_{sat}$ 

Species	Temperature function
$CO_2$	- 0.890+7251/T <sup>2</sup> -1710.6/T+0.004188T+0.000002683T <sup>2</sup> -0.064logT
$CO_2$	-1.449-40536/T <sup>2</sup> -2135.9/T+0.0065639T+0.000002725T2-0.193logT
$H_2S$	13.608+592324/T2-9346.7/T-0.043552T+0.000029164T2+5.139logT
$H_2S$	13.589+590215/T <sup>2</sup> -9024.5/T-0.044882T+0.000029780T <sup>2</sup> +5.068logT
$H_2$	$-1.640 - 124524/T^2 - 777.19/T - 0.0005501T + 0.000007756T^2 - 0.565logT$
$H_2$	$-1.654 - 95456.8/T^2 - 621.84/T - 0.001257T + 0.000007569T^2 - 0.600logT$

The source for the thermodynamic data used to derive these equations is referred to from Karingithi et al., (2010)

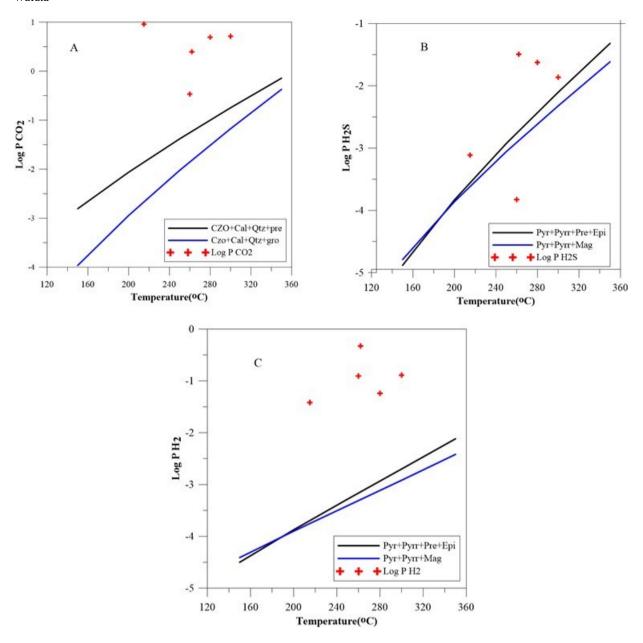


Figure 5: Log Partial pressures of  $H_2S$ ,  $CO_2$  and  $H_2$  in geothermal aquifer water. (A) represents the calculated  $CO_2$  partial pressures at equilibrium with the mineral buffer clinozoisite + calcite + quartz + prehnite and clinozoisite + calcite + quartz + grossular. (B and C) represent the calculated  $H_2S$  and  $H_2$  partial pressures in dilute geothermal fluids at equilibrium with the mineral buffer pyrite + pyrrhotite + prehnite + epidote and pyrrhotite + pyrite + magnetite. These are based on temperature functions from Karingithi et al., (2010).

From figure 5A, the aquifer partial pressure of  $CO_2$  in the wells OW 916, OW 910, OW 905A, OW 904 and OW 904A lie way above the equilibrium mineral buffers. The case is similar for the partial pressures of both  $H_2S$  and  $H_2$  in these wells. Different things could have caused this. The uncertainties associated with the calculation of the aquifer fluid composition and related to the exact equilibrium  $CO_2$  concentration with respect to the mineral buffer reactions could be one of them. Given that the concentration of the aquifer gas composition, especially for the highly soluble gases is influenced by the choice of whether there is initial steam in the aquifer or not. In this case, this choice was not determined. Additionally, the activity of the end member minerals like clinozoisite-Epidote highly influences the mineral reactions that have been applied. From the lithological plot, it was seen that Epidote is the major end member, yet the equation of reaction considers clinozoisite. These uncertainties certainly make it difficult to ascertain which mineral buffer if any at all controls the concentration of these gases.

Another approach was considered where different temperature equations for equilibrium constants were used to plot the mineral buffers. The equations so considered are the empirically derived temperature functions for solute and gas concentrations in geothermal reservoir waters in Iceland as discussed by Stefansson and Arnórsson, (2002). From these data, the same partial pressures of CO<sub>2</sub>, H<sub>2</sub>S and H<sub>2</sub> in these selected wells were plotted as shown in figure 6 below. Table 2 below shows the temperature equations for the equilibrium constants used.

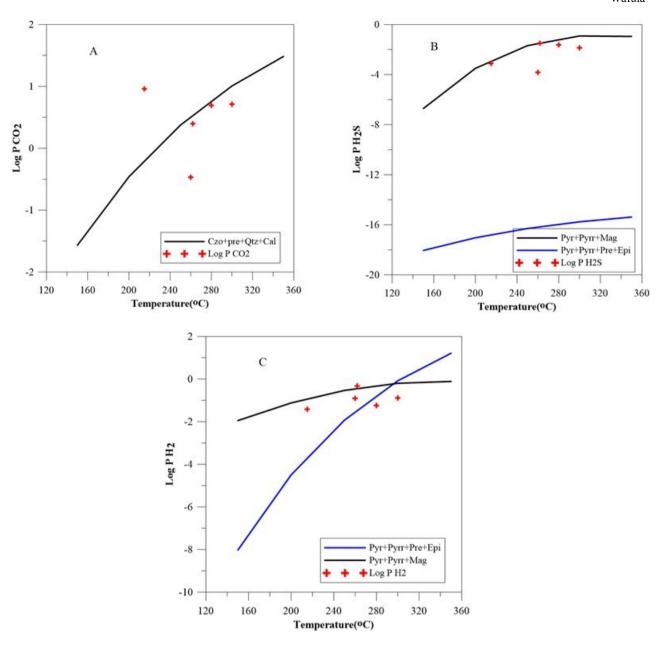


Figure 6: Log Partial pressures of H<sub>2</sub>S, CO<sub>2</sub> and H<sub>2</sub> in geothermal aquifer water. (A) represents the calculated CO<sub>2</sub> partial pressures at equilibrium with the mineral buffer clinozoisite + calcite + quartz + prehnite and clinozoisite + calcite + quartz + grossular. (B and C) represent the calculated H<sub>2</sub>S and H<sub>2</sub> partial pressures in dilute geothermal fluids at equilibrium with the mineral buffer pyrite + pyrrhotite + prehnite + epidote and pyrrhotite + pyrite + magnetite. These are based on temperature functions from Stefansson and Arnórsson, (2002).

Table 2: Empirically derived temperature functions for solute and gas concentrations in geothermal water in Iceland from Stefansson and Arnórsson, (2002)

Species	Temperature Functions
$CO_2$	- 2.81-5012.7/T-0.00919T+6.464logT
$H_2S$	-18.75-24738.9/T-0.10133T+43.170logT
$H_2S$	-2.76-5758.2/T-0.00850T+6.359logT
$H_2$	-10.14-17763/T-0.04084T+23.368logT
$H_2$	-492.53+14263/T-0.09591T+189.4logT

Additional information on the equations can be referred to the text in Stefansson and (Arnórsson, 2002)

From figure 6A above, the partial pressure of CO<sub>2</sub> is in equilibrium with the mineral buffer Clinozoisite+ quartz+ calcite+ prehnite for the wells OW 916 and OW 904 A while Ow 905A and OW 910 are tenths of magnitude far away. From figure 6B the partial pressure of H<sub>2</sub>S for OW 916 is in equilibrium with the mineral buffer Pyr + Pyrr + Mag, while OW 904, OW 904A are slightly off. However, they are all off the mineral buffer Pyr + Pyrr + Pre + Epi, which clearly is not contributing to the concentration of these gases. From figure 6C the partial pressure of H<sub>2</sub> has similar representation as that for H<sub>2</sub>S only that in this case, the data for OW 905A is slightly off the equilibrium line unlike in the H<sub>2</sub>S plot where it was on the line.

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From this data, certain inferences can be made. There could be probably three occurrences of aquifer fluid within the domes area. The major structures controlling fluid movement and flow in the domes area; the Ol-Njorowa gorge, an erosional channel extending for  $\sim 16$  km in total length, an upflow in the southern central side of the domes, and the N-S trending deep seated faults in the area. The aquifer fluid in OW 916 and surrounding wells with similar characteristics is more likely a pure geothermal fluid from depth that has had very minimal or no modification from hence its equilibrium with the mineral buffers. The wells in OW 904 and 904A environs are associated with the modified upflow liquid as well as partioning of the aquifer fluid as it rises hence the high NCG but disequilibrium with the mineral buffer. The wells around OW 905A are purely modified fluids that have direct access to a major structural feeder that is bringing in the high gas content from the upflow zones.

Classification of a geothermal system can be made based on the non-condensable gas (NCG) content because geothermal systems all over the world vary considerably from almost zero to as much as 25% of gas by weight of steam (Geremew, 2012). This can also be applied among different wells within a particular geothermal field in order to classify different reservoir sections. Figure 7 below shows the NCG content of selected wells in the Olkaria domes wells over a period of time. From this data, two different clusters. The first cluster is represented by OW 910 and OW 916. This represents wells in the eastern side of the domes area. These are characterised by lower NCG contents of averagely 0.5 – 0.6 %. The other wells OW 905A, OW 904 and OW 904A are characterised by higher NCG contents of > 1% up to 1.8%. Comparing that to the Log Plot data, it is evident that the depths of the major aquifers in these two areas are different. Therefore, it seems that the wells in this eastern side of the domes are clearly fed from a different aquifer than those from the eastern central side. Knowing that the gas content of geothermal fluids is influenced by numerous process including proximity to outflow and upflow areas, depths to the points of boiling, and the nature of the initial fluid whether it's a one phase liquid or two phase liquid and steam among others, then we can postulate that there are different processes occurring within this sector that are contributing to this differing NCG content within the Domes area.

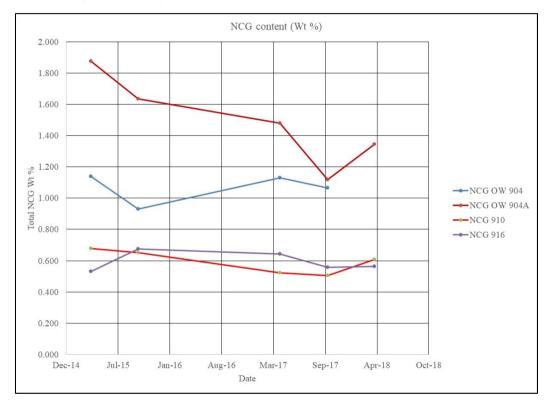


Figure 7: NCG content of representative wells in the Olkaria Domes over a period

## 5. CONCLUSIONS

The wells in the domes area differ in the gas content in the aquifer fluid. The choice of the determination of aquifer fluid composition influences the calculated concentrations of certain components in the aquifer fluid as well as the temperature functions and equations of reactions that are considered. In the domes sector, the partial pressure of gases in some wells is probably in equilibrium with certain mineral buffers while some wells are in disequilibrium. The partial pressure of  $CO_2$  in specific wells is controlled by equilibrium with the mineral buffer clinozoisite + prehnite + calcite + quartz. The partial pressures of  $H_2S$  and  $H_2$  on the other hand are controlled by the mineral buffer pyrite + pyrrhotite+magnetite. The sector could be probably classified into three zones based on these permutations of gas partial pressure and mineral buffers.

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