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ASSESSMENT OF BOILING EFFECTS ON δD AND δ^{18}O COMPOSITION OF GEOTHERMAL RESERVOIR FLUIDS AND THEIR SUITABILITY ON USE AS TRACERS OF ORIGIN OF GEOTHERMAL FLUIDS

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ABSTRACT

A geothermal fluid can boil adiabatically (at constant enthalpy) as the fluid rises to the surface or at constant temperature/pressure (isobaric) due to addition of heat from the reservoir rocks to the fluid. These two modes of boiling cause isotope fractionation between liquid water and the water vapour formed. As a result, the isotope composition of the original fluid is modified and this increases the complexity in interpretation of isotope composition and their use as tracers for the origin of geothermal fluids, especially when the two phases separate in their ascent to the surface. This study evaluates the effects of the two boiling processes for Olkaria geothermal reservoir fluids and their effect on the deuterium and oxygen-18 isotope composition of the geothermal fluid. Two well samples 17-KEN-1 (OW-42) and 17-KEN-14 (OW-732) with a reservoir quartz geothermometer temperature of 236 and 294°C, respectively, and both sampled at 11 bar were simulated for isobaric and adiabatic boiling. The boiling was carried out at temperature and enthalpy steps and at each step, fractionation of deuterium and oxygen 18 assessed. From the results of the model, adiabatic boiling fractionates deuterium and oxygen-18 to a higher extent compared to isobaric boiling. The results of the modelling are presented together with the isotope compositions of wells plotted along the Kenya Rain Line (KRL) in order to give a glimpse into the complexity caused by these reservoir processes in the use of stable isotopes of water as tracers for the origin of geothermal fluid.

1. INTRODUCTION

Olkaria geothermal field is located in southern part of the East African Rift Valley system that passes through Kenya. At present it hosts several power plants operated by three entities (KenGen - Kenya Electricity Generating Company, Ltd., Orpower 4 Inc., and Oserian Development). The field is a high-temperature volcanically hosted geothermal field and lies within the Quaternary Olkaria volcanic complex (Figure 1). It is a multicentre volcano covering a little over 204 km^2 (Clarke et al., 1990). The installed capacity, as at end of 2017, was approx. 670 MWe (Axelsson et al., 2017).

Several studies on deuterium, oxygen-18 and tritium have been carried out on surface waters, shallow ground waters, fumaroles and discharge from geothermal wells (Clarke et al., 1990; Karingithi, 2002;

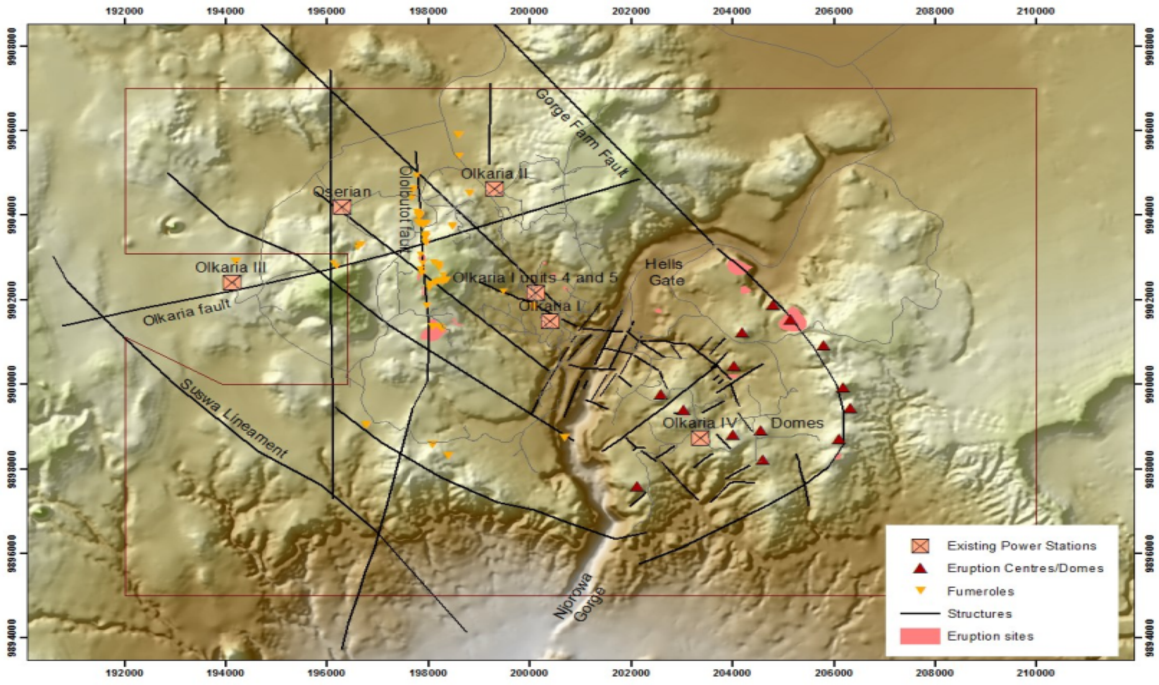

FIGURE 1: Map showing KenGen's geothermal concession area in the Olkaria volcanic complex; also shown in the map are geological structures and geothermal power plants at present (Axelsson et al., 2017)

Karingithi et al., 2010; Nkapiani, 2014; Ojiambo et al., 2005; Ojiambo and Lyons, 1993; Owens et al., 2015). These studies have been aimed at identifying the surface water interaction with rock at near surface, dating the age of the geothermal waters and identifying the source of geothermal water discharged from the geothermal field. Attempts have also been made to identify the mixing patterns of the sources of water discharging from the geothermal wells and to quantify the contribution of each source to the geothermal reservoir. These studies have identified the source of water discharging from the Olkaria geothermal field as a mixture of shallow meteoric recharge from the flanks of the rift valley and a deep axial flow in the rift valley that has undergone evaporation before ground infiltration. There has been no attempt, however, to quantify the effect of reservoir processes like boiling on the stable isotope composition of liquid water and water vapour discharged from the wells so as to evaluate the effect of boiling and the effect on the suitability of deuterium and oxygen 18 as tracers for the origin of the geothermal water.

2. EFFECTS OF BOILING TEMPERATURE, LIQUID WATER VAPOUR FRACTION ON STABLE ISOTOPES

Use of stable isotopes of water to identify the source of water from geothermal reservoirs may be complicated by physical processes occurring in the upflow zones in geothermal systems. High-temperature geothermal systems are at temperatures greater than surface or near surface conditions and as these waters rise, they cool through boiling as a result of the reducing pressure, by conduction or mixing with near surface waters. Only waters that cool by conduction retain their original isotopic composition (Truesdell and Hulston, 1980).

Fractionation of isotopes between liquid water and water vapour depends on the boiling temperature and the ratio of water and steam formed from the boiling. At temperatures below the critical point of water (374°C for pure water), the heavier oxygen isotope (^{18}O) partitions preferentially in liquid water for all temperatures below the critical point. Deuterium, on the other hand, fractionates in the vapour phase at temperatures below the critical point and 221°C showing a maximum at 280°C. Below 221°C, the reverse occurs and the heavier isotope partitions in the water vapour (Truesdell and Hulston, 1980).

If the two phases formed separate, the temperature of boiling and the extent of boiling can produce fluids with different isotopic composition from the same parent. This process can cause variability in the isotope composition of the fluid other than the variability in the sources of the original geothermal fluid.

This study was aimed at quantifying the effects of boiling on the isotopic composition of the fluid by considering two scenarios. These are adiabatic boiling (constant enthalpy) and isobaric boiling (boiling at constant pressure/temperature). Isobaric boiling might occur through addition of heat into the fluid from the rocks which may occur as a result of a temperature gradient that is created between the rocks and the fluid as a result of depressurization boiling (Arnórsson et al., 2007; Karingithi et al., 2010).

3. SAMPLING AND ANALYSIS

Seventeen two-phase well discharge samples were taken in the second half of November 2017 for this study. The selection of the wells to sample targeted wells in upflow zones and those in the periphery of the upflow zones .Upflow zones in Olkaria have been identified based on formation temperature through downhole temperature logs and fluid chemistry (Axelsson et al., 2017; 2013). Variability in well discharge enthalpies and geological structures in the field were also considered. The sampling was done according to procedures for sampling wet steam wells as described in Arnórsson et al. (2006). Steam and water samples were collected using a webre separator connected to the two-phase line from the well. The webre separator was flashed for at least 5 min, shut and the pressure and temperature in the webre separator recorded.

Samples of the vapour phase were collected in pre-evacuated gas bulbs containing about 5-10 mL 50% KOH. A sample of the steam was then cooled and 10 mL of sample collected in high-density polyethylene vials, filled to the top and tightly capped for isotope analysis. For liquid phase, the water was cooled down in-line using a cooling coil. Samples for pH, CO_2 and H_2S determination were collected into glass flasks. For major elements, the liquid water was filtered through 2 μm pore filter paper using a Nalgene 300-4000 vacuum filter holder. The filtered water sample was divided into three parts, a sample was collected in 40 mL high-density polyethylene (HDPE) plastic bottle to which 0.4 mL of 67% HNO_3 (ultraclean) was added, for major cation analysis. The second aliquot was collected in a 40 mL HDPE plastic bottle, with no further treatment for anion analysis. The second aliquot was collected in a 40 mL HDPE plastic bottle to which zinc acetate was added to precipitate H_2S for SO_4 analysis. A 10 mL sample for isotope determination was also collected for the liquid phase.

For the liquid phase, dissolved H_2S was analysed on site by Hg-precipitation titration using dithizone as an indicator (Arnórsson et al., 2006). pH and CO_2 was analysed within few days using a combination electrode and modified alkalinity titration (Stefánsson et al., 2007). The concentrations of major cations (SiO_2, B, Na, K, Ca, Mg, Al, and Fe) were determined using an ICP-OES, whereas major anions (F, Cl and SO_4) were analysed using IC. The precision of the measurements based on duplicate analysis at the 95% confidence level was generally $< 3\%$.

For the steam phase, the concentration of H_2O was determined gravimetrically, and the concentrations of CO_2 and H_2S using modified alkalinity titration and Hg-precipitation titration as described above. The concentration of non-condensable gases (N_2, H_2, CH_4 and O_2) were determined using a GC system. From these analyses, the mole fractions of gases in the steam phase including H_2O were calculated. The analytical uncertainty has been estimated based on standard analysis to be within 10%. The samples for deuterium (D) and oxygen-18 (^{18}O) in both liquid water and water vapour were analysed with Delta V Advantage Isotope Ratio Mass Spectrometer. The results are reported in ‰ relative to Vienna-Standard Mean Ocean Waters (V-SMOW) based on reporting standards for concentration of D and ^{18}O of Craig (1961)

4. RESULTS AND DISCUSSION

Reconstruction of the aquifer fluid composition was carried out using the WATCH speciation program (Arnórsson et al., 1982; Bjarnason, 2010) from major element analysis of the samples. For these calculations, conservation of mass and enthalpy was assumed according to (Arnórsson et al., 2007). The enthalpy of the discharge fluid was taken as the enthalpy of saturated fluid at the reservoir temperature calculated from quartz geothermometer (Fournier and Potter, 1982). The calculated aquifer fluid composition is given in Table 1 and the isotope composition of the surface discharge fluid is given in Table 2.

The effect of boiling on isotope composition of aquifer fluid was simulated by boiling the fluid with the aid of the WATCH program in order to assess the isotope composition evolution of the liquid water and the water vapour as boiling occurs. The aquifer fluid was boiled in two ways. One by adiabatic boiling in which the enthalpy of the fluid was held constant and the fluid boiled in temperature steps from the reservoir fluid temperature to 100°C to simulate ascent of fluid to the surface. In the second method, the reservoir fluid temperature or pressure (isobaric) was held at the reservoir temperature and the enthalpy of the fluid increased from the enthalpy at the reservoir temperature up to 2750 kJ/kg in steps of 50 kJ/kg. The two boiling processes are illustrated in Figure 2.

Two well samples were simulated for boiling, 17-KEN-1 (OW-42) and 17-KEN-14 (OW-732) with aquifer temperatures of 236 and 295°C, respectively. Both wells were sampled at 11 bars. The isotope compositions of the two wells were calculated from the surface measurement using liquid enthalpy at the quartz geothermometer temperature and steam fraction at collection using fractionation factors from (Horita and Wesolowski, 1994). The reservoir fluid composition was then simulated for isobaric and adiabatic boiling. At each boiling step in the two methods, the isotope composition was calculated for the water vapour and liquid water formed. For the adiabatic boiling, both temperature and the steam fraction were changing at each step while for the isobaric boiling only the steam fraction was changing as a result of the addition of heat at constant temperature. The isotope calculations were carried out using IsoGem - v0.5 program.

TABLE 1: Aquifer fluid composition at calculated enthalpy (concentrations are in mg/kg)

Sample no.	Well no.	TQtz[1]	TNaK[2]	pH	B	SiO_2	Na	K	Mg	Ca	F	Cl	SO_4	Al	Fe	CO_2	H_2S	H_2	CH_4	N_2
17-KEN-1	OW-41	237	302	6.54	0.00	412	168	42	0.027	0.44	64.88	105	4.2	1.832	0.045	786	23.8	5.20	0.17	2.28
17-KEN-2	OW-725	234	223	6.49	2.12	398	395	48	0.022	0.58	36.34	254	0.0	1.222	0.219	2167	205.5	10.81	1.81	6.33
17-KEN-4	OW-37A	261	310	7.65	6.60	544	847	236	0.012	0.25	139.9	1055	89.9	0.500	0.014	525	66.3	4.05	0.78	20.35
17-KEN-5	OW-44A	264	318	6.80	26.47	529	519	154	0.019	0.6	64.4	750	36.4	1.024	0.013	843	23.6	6.77	0.96	7.23
17-KEN-6	OW-907A	263	257	6.82	1.30	525	260	44	0.020	0.4	41.2	103	14.6	1.137	0.018	4749	15.3	7.35	4.49	7.05
17-KEN-7	OW-910	272	280	7.53	2.58	577	338	70	0.007	0.18	107.3	201	7.7	0.687	0.021	1226	32.7	8.33	1.19	4.13
17-KEN-8	OW-35	274	287	6.94	8.30	577	466	102	0.021	0.37	69.3	515	19.4	1.545	0.016	3680	21.6	21.28	1.95	7.47
17-KEN-9	OW-910B	262	266	7.47	1.48	533	331	60	0.020	0.38	46.92	114	12.9	1.186	0.023	1784	67.4	5.88	1.86	6.22
17-KEN-12	OW-714	257	248	6.96	2.09	500	406	63	0.019	0.4	57.44	354	24.9	1.143	0.016	2156	137.8	9.19	1.92	8.33
17-KEN-13	OW-916A	276	284	7.25	2.85	588	426	91	0.019	0.44	179.2	215	5.5	0.927	0.020	2096	30.9	11.89	5.13	4.45
17-KEN-14	OW-732	295	301	7.21	2.58	659	315	78	0.023	0.56	39.02	356	4.5	1.229	0.039	2606	95.9	19.78	4.33	16.22
17-KEN-15	OW-42	259	276	6.34	38.74	506	128	25	0.024	0.74	28.28	169	8.0	3.448	0.213	602	23.7	2.90	0.21	3.11
17-KEN-16	OW-720	236	215	7.11	1.86	412	372	43	0.020	0.5	52.44	222	54.6	0.870	0.021	925	80.3	5.54	0.87	5.9
17-KEN-17	OW-904	253	252	7.07	1.29	487	382	61	0.025	0.47	44.5	104	11.0	1.026	0.023	3607	58.5	9.83	8.39	6.19

[1]Fournier & Potter, 1982; [2]Arnórsson et al., (1983)

TABLE 2. Deuterium and oxygen 18 composition of steam and water samples collected

Sample	**Well**	**T (°C)**	**Ps (bar)**	**Enthalpy (kJ/kg)**	**δD-H_2O (liquid) (‰)**	**δ^{18}O-H_2O (liquid) (‰)**	**δD-H_2O (vapour) (‰)**	**δ^{18}O-H_2O (vapour) (‰)**
17-KEN-1	OW-41	184	10.9	2747	5.9	2.8	6.2	1.3
17-KEN-2	OW-725	156	5.5	2180	14.3	2.1	5.3	-0.9
17-KEN-3	OW-735*	173	8.3	2240	9.5	1.7	2.1	-1.3
17-KEN-4	OW-37A	187	11.5	2670	0.8	0.8	-3.2	-1.5
17-KEN-5	OW-44A	183	10.7	1786	2.2	2.2	-0.2	-0.1
17-KEN-6	OW-907A	185	11	2049	9.0	1.5	6.7	-0.6
17-KEN-7	OW-910	205	17	2301	8.9	2.3	7.1	0.2
17-KEN-8	OW-35	196	14	1756	2.9	1.3	-0.9	0.0
17-KEN-9	OW-910B	199	15	1754	6.4	1.7	4.6	-0.3
17-KEN-10	OW-909*	187	11.5	2144	10.1	2.7	4.7	0.2
17-KEN-12	OW-714	158	5.7	1725	12.8	1.9	3.9	-0.7
17-KEN-13	OW-916A	185	11	2718	16.1	3.2	9.0	0.6
17-KEN-14	OW-732	185	11.1	2287	10.2	1.8	4.5	-0.5
17-KEN-15	OW-42	187	11.46	1568	11.1	2.7	7.4	0.7
17-KEN-16	OW-720	165	6.78	2747	12.7	1.4	4.9	-1.2
17-KEN-17	OW-904	185	11	2180	12.9	2.1	6.2	-0.6

*composition calculated using TNa-K geothermometer Arnórsson et al. (1983)

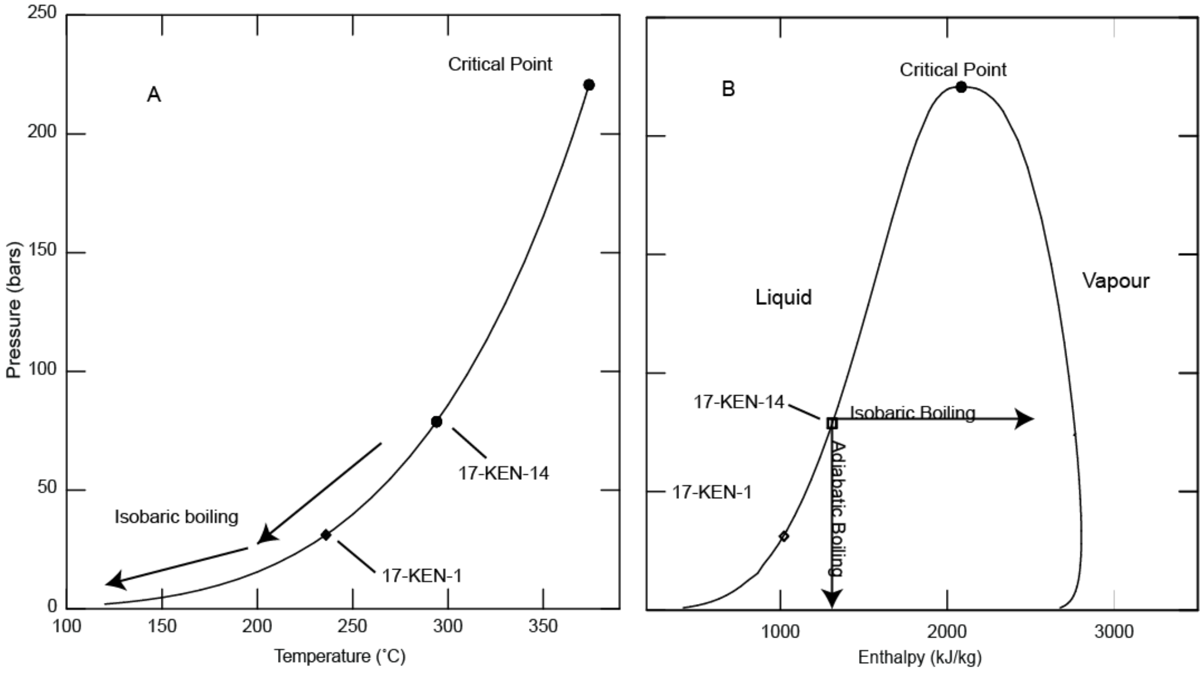

FIGURE 2: (A) A P-T relationship of the fluid from the well is shown, adiabatic boiling follows the curve from the reservoir temperature to 100˚C; (B) A pressure-enthalpy relation is shown with path for adiabatic boiling (constant enthalpy) and isobaric boiling (constant pressure)

The results of the modelling of deuterium and oxygen-18 upon boiling are shown in Figure 3. The local meteoric line, Kenyan Rain Line (KRL) developed by Allen et al., (1989) is plotted in the figure for reference. In the model, adiabatic boiling causes fractionation of deuterium in reservoir fluid for 17-KEN-14 from a reservoir value for δD 8.7‰, the value ranges between 8.7‰ and 12‰, while for δ^{18}O with a reservoir composition of 1.19‰, it ranges from 1.19‰ to 3.2‰, for liquid water and water vapour. For 17-KEN-1, δD (with reservoir δD = 5.94) ranges from 5.94‰ to -14.5‰ and δ^{18}O (reservoir fluid δ^{18}O= 2.62) ranges between 2.62‰ and -1.11‰. Isobaric boiling causes a similar fractionation but the fluid follows a straight path of evolution.

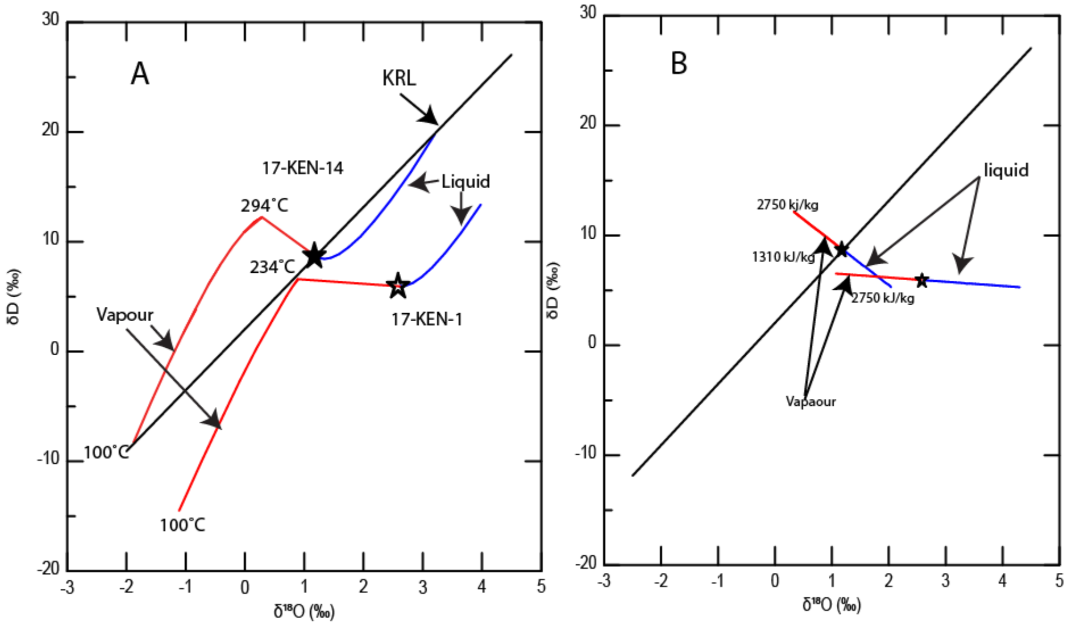

FIGURE 3: Model results showing steam and water isotope evolution upon adiabatic boiling and isobaric boiling on aquifer fluids of 17-KEN-1 (δD= 5.94‰, δ^{18}O =2.62‰) and 17-KEN-14 (δD= 8.7‰, δ^{18}O =1.19‰); (A) shows isobaric boiling, the evolution of the isotope composition of the steam is shown by the red line while that of water is shown by the blue line; in (B) isotope evolution upon isobaric boiling is shown.; the Kenya Rain Line (Allen et al., 1989) is plotted

Sample 17-KEN-14 has higher reservoir temperatures (294˚C) than 17-KEN-1 and deuterium has a different fractionation trend, the first steam that forms is heavier considerably heavier. A comparison on the of D and ^{18}O isotope evolution model results for the two wells and steam and water isotope composition is shown in Figure 4.

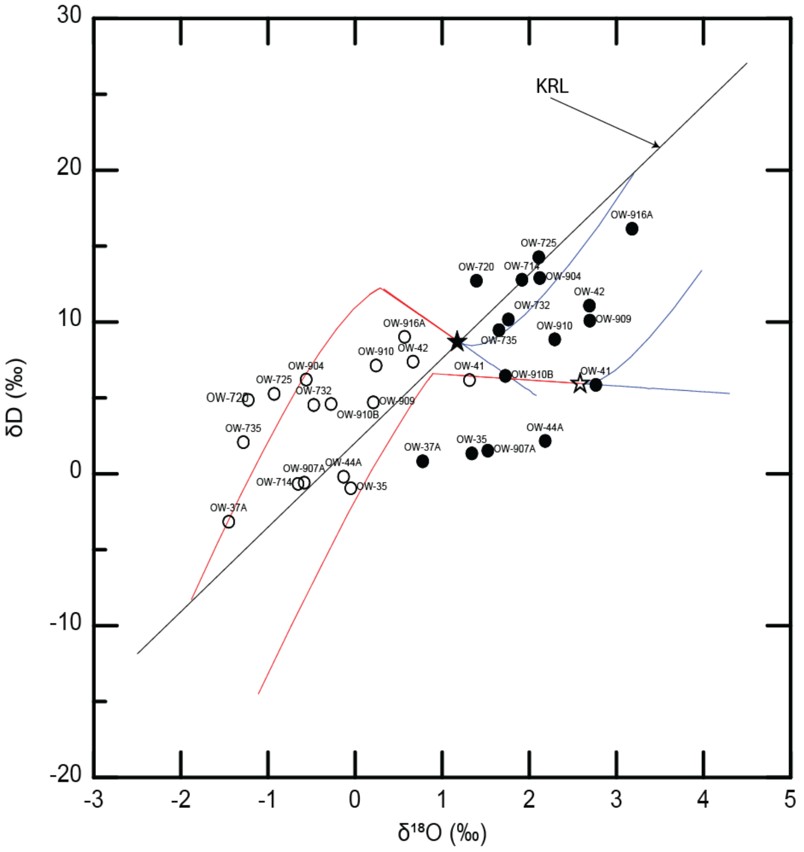

FIGURE 4: Steam and water isotope composition from two-phase fluid analysis for the wells samples; open circles are steam isotope composition and closed circles are water isotope composition

5. CONCLUSIONS

The mode of boiling of geothermal fluids and reservoir temperature plays a role in the extent of fractionation of D and ^{18}O. At high temperatures, above 221°C, steam formed is enriched with deuterium relative to the fluid. Adiabatic boiling fractionates deuterium and ^{18}O between the two phases to a large extent and the resulting fluid may have a large isotope range or causes more variability than the source of the fluid recharging the reservoir may have. Separation of the phases after formation during their ascent to the surface may further cause more variability in the fluid that may not reflect the source and as a result complicate the use of stable isotopes of water as tracers of origin of geothermal fluids. The results of isotope composition in geothermal well discharges need to be treated with care so as not to give misleading conclusions as even a source with distinct isotope composition can give rise to fluids of variable isotope composition caused by reservoir processes.

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