GEOCHEMICAL INTERPRETATION OF THERMAL WATER AND GAS SAMPLES FROM KRISUVIK, ICELAND AND ALID, ERITREA

Ermias Yohannes Berhane
Ministry of Energy and Mines
Department of Mines
P.O.Box 272, Asmara,
ERITREA

ABSTRACT

Alid, Eritrea is one of the geothermal fields located within plate tectonic rift zones; an environment characterized by high heat-flow. In this paper, geochemical data of the system is reviewed and interpreted. The objective of this study is to explore the potential of geochemical methods to predict the reservoir temperatures and evaluate equilibrium conditions for the Alid fields.

The Alid water samples are characterized by low pH and high sulphate content, typical of steam heated surface waters. As a result, solute geothermometers do not represent temperatures of the geothermal reservoir. This is reflected by low quartz geothermometer temperatures (80-224ºC) compared to the gas-thermometer temperatures that range between 163 and 364°C with an average of 272ºC. The results indicate that the geothermal reservoir at Alid is vapour-dominated and surface thermal waters are derived from shallow, steam heated ground water reservoirs.

1. INTRODUCTION

At constructive plate boundaries, new crust is formed by volcanic activity. The new thin crust is characterized by high heat flow due to the volcanic activity and by extensional tectonics, thus providing the right conditions for high temperature geothermal activity. The African Rift valley is among the constructive margins in the world that bear numerous sites of geothermal activity. Kenya is a notable example of the African Rift that harnesses the geothermal energy. Eritrea, which lies on the northern portion of African Rift, may have similar prospect of geothermal potential, evidenced from the presence of good surface manifestations.

This study presents geochemical evaluation of the conditions of mineral equilibria and estimation of subsurface temperatures from geothermal fluids of selected hot springs and fumaroles of Alid geothermal field, Eritrea. Geochemical methods provide powerful efficient and relatively inexpensive tools for assessing reservoir temperature through analysing surface samples. Geochemical exploration is, therefore, very important in the early stages of evaluation of geochemical systems since reservoir temperature is the main factor that determines the potential use of a particular geothermal resource (Arnorsson, 2000).

Alid is located at the northern part of the African Rift valley close to where the active continental rifting culminates into sea floor spreading, Red Sea (Figure 1). It runs approximately NNW-SSE and continues conspicuously to the south, which eventually intercepts the Afar triple junction. This zone has been seismically, tectonically and volcanically active throughout the Late Holocene and Quaternary (Williams et al., 2004). Manifestations of rift succession occur in the form of faults, tensional fissures and volcanic activity. This zone of the rift is influenced by the presence of the Afar hot spot (Mohr et al., 1978).

The Alid geothermal field has been recognized as potential high enthalpy geothermal resource for several decades due to the evidence of various surface manifestations and the presence of magma within the context of spreading related basaltic volcanism (UNDP, 1973; Beyth, 1994). The first preliminary assessment was carried out by Angelo Marini in 1901 (Marini, 1938). In 1996 a team from the USGS and Eritrean counterparts assessed the geothermal potential of Alid through geological mapping, geochronology and geochemical sampling (Clynne et al., 1996, Lowenstern et al., 1999). This study makes use of the geochemical data collected in the 1996 field expedition.

2. SAMPLING AND METHODS OF ANALYSIS

In this study, both gas and water samples from Alid collected during 1996 are evaluated. Water samples were collected in polyethylene bottles of 500, 250 and 125 ml. Samples for cation and SiO_2 determinations were acidified with HNO_3. Before acidification, the samples were filtered with a 0.45 µm pore size membrane. Outlet temperature and pH were determined directly in the field. Standard procedure as outlined by Giggenbach and Goguel (1989) and Fahlquist and Janik (1992) were used for sample collection in Alid. Fumarole samples were collected for steam and non-condensible gases including CO_2, H_2, CH_4, H_2S, NH_3 and N_2 and Ar. A 1 meter long titanium tube was placed on the fumarole covering the cracks and any outlet with mud to minimize air contamination and ensure steam and gas flow. A Giggenbach bottle partly filled with NaOH solution is attached to the tube using temperature resistant silica plastic tubing. Steam and soluble gases condensed within the tube and flowed to the bottle together with bubbles of non condensable gases. According to the procedures of Fahlquist and Janik (1992) gas chromatography was used for analyses H_2, He, N_2, Ar, and CH_4, monometry for CO_2, gravimetry for H_2S analysis and gas sensing electrodes for $NH_{3.}$ Analyses were conducted at the USGS geothermal laboratory in Menlo Park, California.

3. GEOLOGIC AND GEOTHERMAL SETTING OF ALID GEOTHERMAL FIELD, ERITREA

3.1 Geology of Alid

Alid is part of the Danakil depression a region of active volcanism and high heat flux. Alid volcanic centre is located on the axis of the main rift that radiate NNW from the main triple junction of the Afar triangle (Figure2; Lowenstern et al., 1999). Alid Mountain located in a depression bounded by the Danakil horst to the east and the Eritrean plateau to the west, which rises above 2000 m.a.s.l. The Precambrian basement and granites, covered with Mesozoic to Tertiary sediments and Tertiary basalt, underlain bordering the rift shoulders. Pliocene to Quaternary rift succession mainly lava and minor sediments cover the depression.

Alid volcanic centre is an elliptical structural dome that rises up to 700 m above the adjacent plains of the surrounding lowlands. The oldest rock of Alid volcanic center is a Precambrian mica and kyanite schist that crops out only in a small area of the dissected canyon that drains the east side of the mountain, (Clynne et al., 1996). Sedimentary succession consisting mainly of marine siltstones and sandstones, gypsum beds, fossiliferous limestones, and pillow basalts and sub-aerial basalts overlie the basement. Pliocene or, more likely, Pleistocene is the inferred age of all these lithologies.

Up to 1000 m of structural doming, which began less than about 36 ka caused considerable swelling of the dome resulted in land sliding and collapse of the central region. Fractures associated with deformation are apparent on aerial photographs. The NNW faults are in agreements with the major structural trend of the rift.

3.2 Geothermal manifestation

Surface manifestations of geothermal ground occur in the area in the form of fumaroles and hot springs. Eleven geothermal sites have been identified, of which six are selected for sampling of gas and water (Lowenstern et al., 1999). Ilegedi, Darere and As´ela are the foremost ones with the earlier being the largest and most prominent. Owing to lack of fumarolic venting, Ghinda, Docholo and Dibara were not sampled although the respective temperatures of springs reach to 93°C, 90°C, and 80°C. The fumaroles and boiling pools are evenly distributed irrespective to the lithological units: rhyolithic breccia (Abakri, As´ela, Darere), the sedimentary sequence (Humbebet), and Precambrian basement rocks (Ilegedi). Thus the various lithological units do not seem to control the distribution of the geothermal surface manifestation. However the flow movement for the formation of the pools appears to be controlled by fractures as most of the fumaroles and alteration zones occur in alignment.

White and red clays, white and yellow crustose sublimates and fine grained white and green sublimates are the common alterations occur with the sublimate minerals are found to be ammonium hydrates and sulfates (Beyth, 1996). Anhydrite, Kalinite/alum [$KAl(SO_4)_2.11H_2O$], tchermigite [$(NH_4)Al(SO_4)_2.12H_2O$], montmorillonite and illite occur among other alteration minerals.

4 GEOCHEMISTRY OF ALID THERMAL WATER AND GAS SAMPLES

4.1 Chemical composition of Alid samples

Table 1lists the chemical analysis of the water samples of Alid. These hydrothermal samples collected from Alid are from pools except for Humbebet, which is a drip. Data obtained from gas analyses are reported in Table 9. All of the samples contained over 95% steam except for the bubbling pool of Ilegedi 3 (sample ELG96-5), where significant condensation had occurred.

Since the chlorine content is low, ranging from 0.14 to 20.9 ppm, it is advisable to use the anion Cl-SO_4-HCO_3 ternary diagram (Figure 3) as the basis of initial classification (Giggenbach, 1991). Accordingly the Alid water samples are classified as steam heated water, with one exception that falls in the field of HCO_3- rich waters. This is consistent with low pH values of water (ELW96-5 and 6 with respective pH values of 5 and 3. The high SO_4^{2-} content and low pH of steam-heated water is a result of near surface oxidation of H_2S proceeding from deep reservoir zone resulting in the formation of H_2SO_4 (sulphuric acid).

Binary plots of Alid water samples presented in Figure 4, illustrate some of the characteristics of steam-heated waters. The chlorine concentration of the water samples are very low, ranging from 0.14 to 21 ppm whereas the concentration of other elements do not exhibit systematic trends. The Na versus chlorine plot shows a possible positive correlation of these elements. The line fit for this molar plot corresponds to a Cl/Na ratio of about 0.1 or significantly below the halite dissociation line (Cl/Na ratio 1) and far below the sea water-meteoric water mixing line (Minissale et al., 2003). Chlorine is a conservative component in geothermal solutions, i.e., the concentration of this element will increase continuously during the progressive rock dissolution. The very low Cl concentrations indicate that the fluids have not interacted extensively with the bedrock, i.e., they do not represent mature geothermal fluids. Elevated concentration of other components are due to rapid dissociation of the bedrock in the highly acidic steam-heated waters, i.e., they do not represent equilibrium concentrations corresponding to some reservoir condition rather the extent of bedrock dissolution that has occurred at the surface. Consequently, the application of solute geothermometers, mineral saturation calculations, and mixing models to the surface solutions from Alid will not provide information on the conditions in the underlying geothermal reservoir. However, it can be informative to compare predicted reservoir temoeratures for Alid using gas geothermometers to those predicted by solute geothermometers in order to evaluate the magnitude of the potential error that could result from making use of steam heated surface waters for deep geothermal solutions.

Table 1 Chemical composition of Alid hydrothermal water samples in ppm.

Sample	locality	T(°C)	pH	SiO2	Na	K	Ca	Mg	Li	NH4
ELW96-5	Ilegedi 1	50	5	195	18.2	11.4	101	31.2	0.02	213
ELW96-6	Ilegedi 2	35	3	402	18.3	132	114	23.5	0.02	105
ELW96-7	As´ela 1	54	7	114	233	20	396	27.2	0.05	15.9
ELW96-8	As´ela 2	57	7	71	213	17	251	21.7	0.04	5.8
ELW96-9	Ilegedi 3	66	6	99.1	11.4	12	157	37.4	0.02	190
ELW96-10	Humbebet	<60	7	39.8	2.86	1.18	111	10.2	0	30.4
Cold water	Buya well	33		54.3	69.7	32.7	126	73.9	0.1	0.1

Sample	Fe	Mn	Cl	SO4	HCO3	F	B	TDS
ELW96-5	10.1	3.11	2.99	1094	0	0.45	0.022	1695
ELW96-6	19.7	3.2	1.19	1767	0	0.21	0.031	2606
ELW96-7	0.04	0.56	20.9	1475	100	0.49	0.049	2417
ELW96-8	0.17	0.24	12.4	1068	66	0.43	0.044	1748
ELW96-9	0.82	3.04	0.84	949	171	1.18	0.015	1633
ELW96-10	<.01	<.01	0.14	74.3	263	0.04	0	572
Cold water	<.01	<.01	59	458	258	0.99	0.33	1195

Table 2. Chemical data of gas samples in mole % of Alid.

Sample	CO2	H2S	H2	CH4	N2	Ar	Gas/Steam*
ELG96-2	97.93	0.219	1.093	0.225	0.412	0.0054	0.0448
ELG96-3	95.53	0.876	2.498	0.132	0.598	0.0126	0.0196
ELG96-4	98.2	0.749	0.503	0.061	0.473	0.0116	0.0259
ELG96-5	95.89	0.662	2.624	0.144	0.653	0.014	1.701
ELG96-6	98.89	0.143	0.605	0.085	0.209	0.0047	0.0565

* Gas/steam ratio is moles total non condensable gas devided by moles H_2O

5.4 Geothermometry of Alid water and gas samples

As noted above the natural geothermal solutions that are available on the surface at Alid are dominated by acid sulphate water; therefore the gas geothermometer is the best method of predicting subsurface reservoir temperature (Goff and Janik, 2000). The calculated values of the geothermometers are presented in Table 3 and depicted in Figure 5. The CO_2 value and H/Ar of Arnorsson and Gunnlaugusson (1985) and Giggenbach (1991), respectively display similar results, which are higher than for other gas geothrmometers. One sample, from the bubbling pool, has a calculated temperature of 561°C using the CO_2 geothermometers. This extremely high value is due to steam condensation in the pool, which dramatically increases the gas/steam ratio. The average gas thermometer temperatures for the sample (excluding the sample from the bubbling pool) range from 250 to 281°C. The calculated values using the CO_2/H_2 of Arnorsson and Gunnlaugusson (1985) and D´Amore and Panichi (1980) geothermometers are quite low ranging, respectively, from 164 to 207°C and 206 to 263°C.

The six gas samples of Alid were plotted in the CO_2-Ar versus H_2-Ar equilibration diagram (Figure 6; Giggenbach, 1991). All of them plot on the vapour equilibrium zone. This indicates that the anticipated hydrothermal system underlying below is a vapour dominated, high enthalpy geothermal reservoir. The temperature plotted ranges from 200 to 275°C, which is in reasonable agreement with the average gas geothermometer temperatures.

Table 3. Calculated temperatures of Alid water samples using various silica geothermometer

Sample	$C0_2$	H_2S /H_2	H_2S	H_2	CO_2 /H_2	AP	H_2/Ar	Aver.
ELG96-2	356	332	221	268	181	218	336	273
ELG96-3	330	322	237	268	206	266	336	281
ELG96-4	339	297	240	245	159	225	290	256
ELG96-5	561	328	355	343	207	263	334	342
ELG96-6	364	329	216	262	164	206	323	266

$C0_2$, H_2S/H_2, H_2S, H_2, and CO_2/H_2 are from Arnorsson and Gunnlaugsson (1985), ^{AP}geothermometer of D´Amore and Panichi, and H_2/Ar is the geothermometer of Giggenbach (1991).

Silica geothermometers were applied to the Alid water samples. The results are shown in table 4 and depicted on Figure 7. Inspection of table 4 shows that the average predicted silica temperatures of the surface samples range from 87 to 225^{0}C. This result is significantly lower than predicted by the gas geothermometers as expected, considering the steam heated nature of the Alid water samples. It is interesting too note that the two samples that yield the highest silica temperatures. ELW96-6 and ELW96-5 do also have the lowest pH values, 3 and 5, respectively. This is further evidence for these waters and illustrates that the high silica concentration of these samples is due to rapid rock dissolution in the very acidic environment, but not equilibrium with quartz at high temperature.

Table 4. Calculated temperatures of Alid water samples using various silica geothermometer

Samples	F ^{1}	F ^{2}	FP^4	A^5	A^6	VS^7	Average	F^8	A^9
ELW96-5	178	167	173	170	159	179	171	157	151
ELW96-6	233	211	229	234	210	233	225	222	209
ELW96-7	145	139	139	133	129	145	138	119	117
ELW96-8	119	117	114	106	105	119	113	90	90

ELW96-9	137	132	132	125	122	137	131	110	108
ELW96-10	91	94	88	77	79	92	87	61	63

The superscript denotes F^1 and F^2 for Fournier (1977) Equation 1 and Equation 2, respectively, FP^4 for Fournier and Potter, (1982), A^5 and A^6 for Arnorsson, (2000) Equation 3 and Equation 4 respectively as mentioned below, VS^7 for Verma and Santayo (1997), F^8 and A^9 for Fournier (1977) chalcedony and Arnorsson et al. (1983), respectively.

Quartz –no stream loss $T°C = \frac{1309}{5.19 - \log S} - 273.15$ ……………………………….Equation (1)

Quartz maximum steam loss at 100°C $T°C = \frac{1522}{5.75 - \log S} - 273.15$ ………………....Equation (2)

Quartz $T°C = -53.5+0.11236\boldsymbol{S}-0.5559\mathrm{x}10^{-4}\boldsymbol{S}^2+0.1772\mathrm{x}10^{-7}\boldsymbol{S}^3+88.390\log\boldsymbol{S}$……….. Equation (3)

Quartz $T°C = -55.3+0.36590\boldsymbol{S}-5.3954\mathrm{x}10^{-4}\boldsymbol{S}^2+5.5132\mathrm{x}10^{-7}\boldsymbol{S}^3+74.360\log\boldsymbol{S}$…………Equation (4)

6. CONCLUSIONS

The Alid water samples are characterized by low pH and high sulphate, typical of steam heated surface waters. As a result, solute geothermometers do not represent temperature of the geothermal reservoir. This is reflected by low quartz-geothermometer temperatures (80 to 224^0C) compared to gas-geothermometer temperatures that range between 163 and 364 with an average of 272^0C. The result indicated that the geothermal reservoir at Alid is vapour-dominated and surface thermal waters derive from shallow, steam heated ground water reservoirs.

The calculated temperatures of the quartz geothermometers and the convergence of the mineral equilibrium for Alid geothermal field are by far below than the calculated gas geothermometers. This shows that the calculated temperature and convergence temperature may reflect the partial equilibrium where the system may be influenced by an introduction of cold water and/or rock water interaction in the up flow zone.

In order to visualize the underground conditions of Alid, a conceptual model is proposed based on the geochemical so far outlined (Figure 8). Meteoric water as a source (Lowenstern et al., 1999) descends down deep into the reservoir and magma heats it mainly by conduction and probably convection with some elements, where the vapour dominated phase in turn heats the aquifer above which develops into steam dominated zone. The water rises up towards the surface as fumaroles or hot springs along the main fracture system mixed with the ground water.

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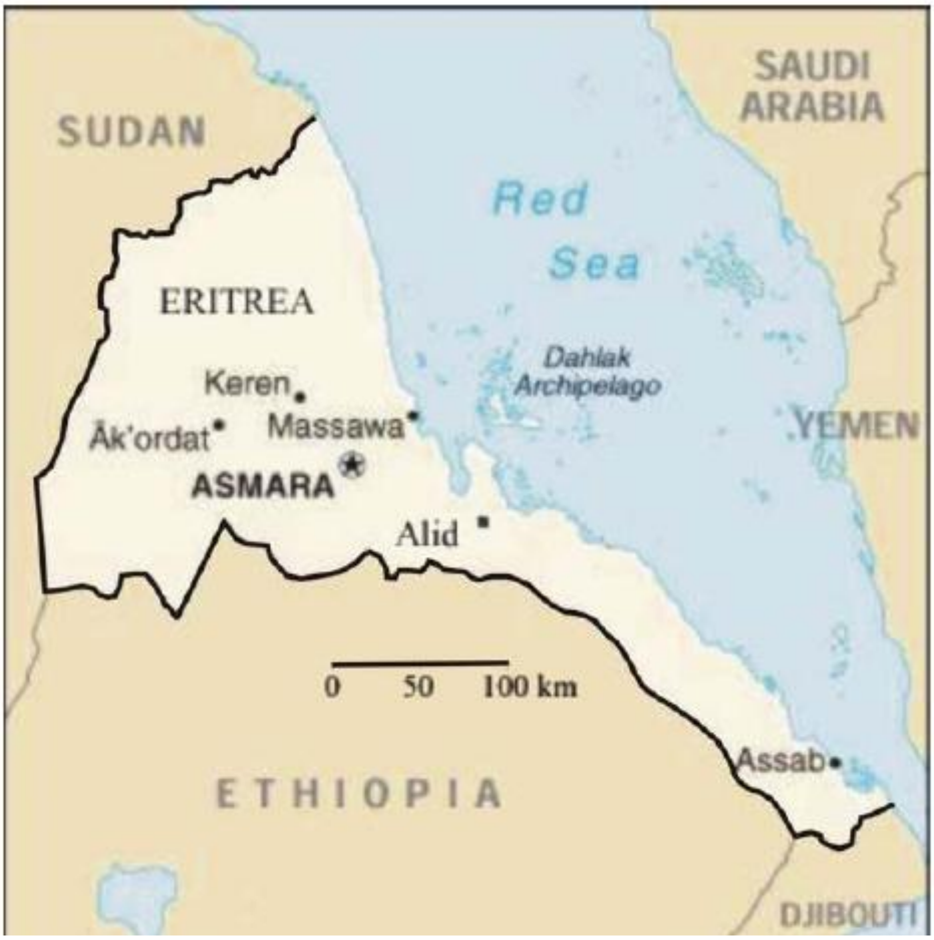

Figure 1. Location map of Alid

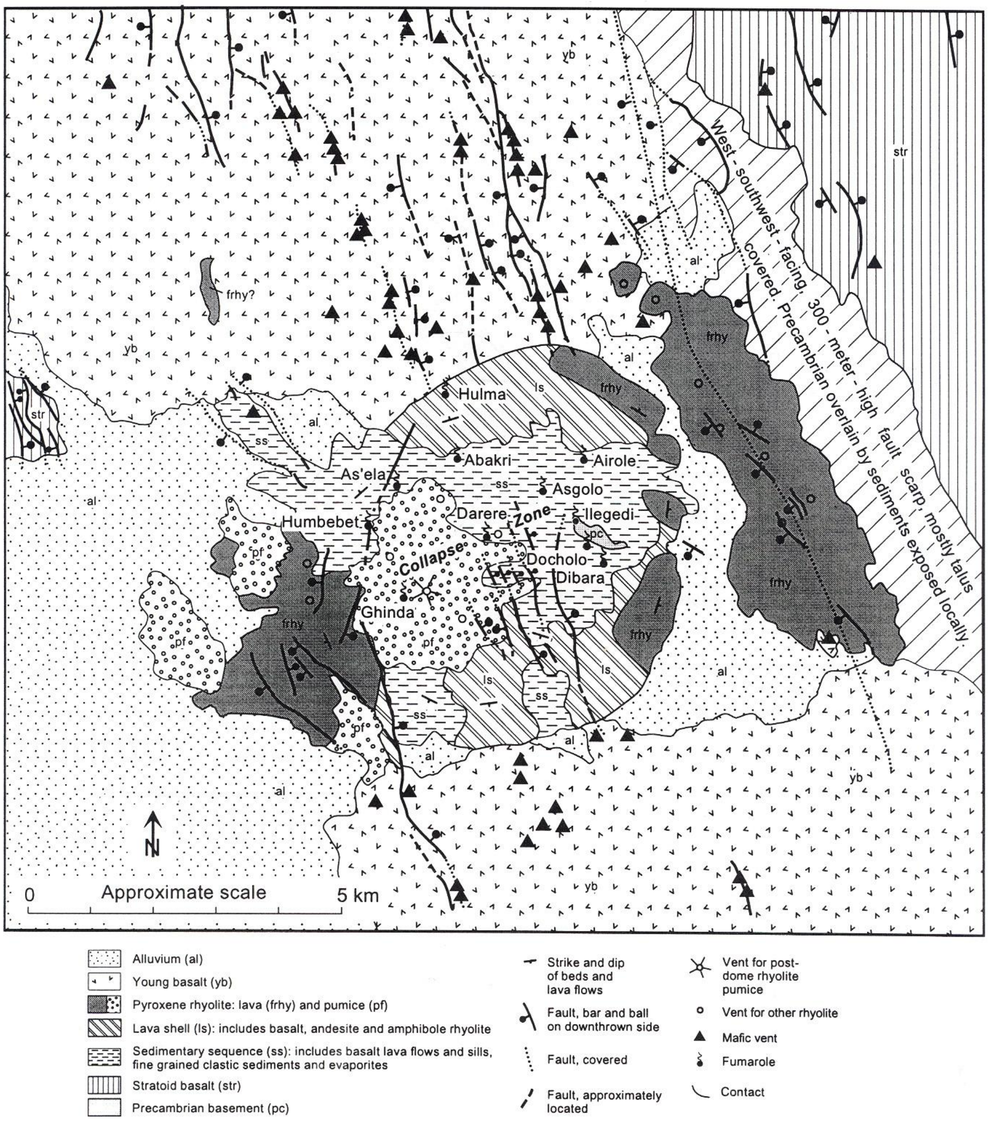

Figure 2: Geological map and sample location map of Alid volcanic centre (Clynne et al., 1996)

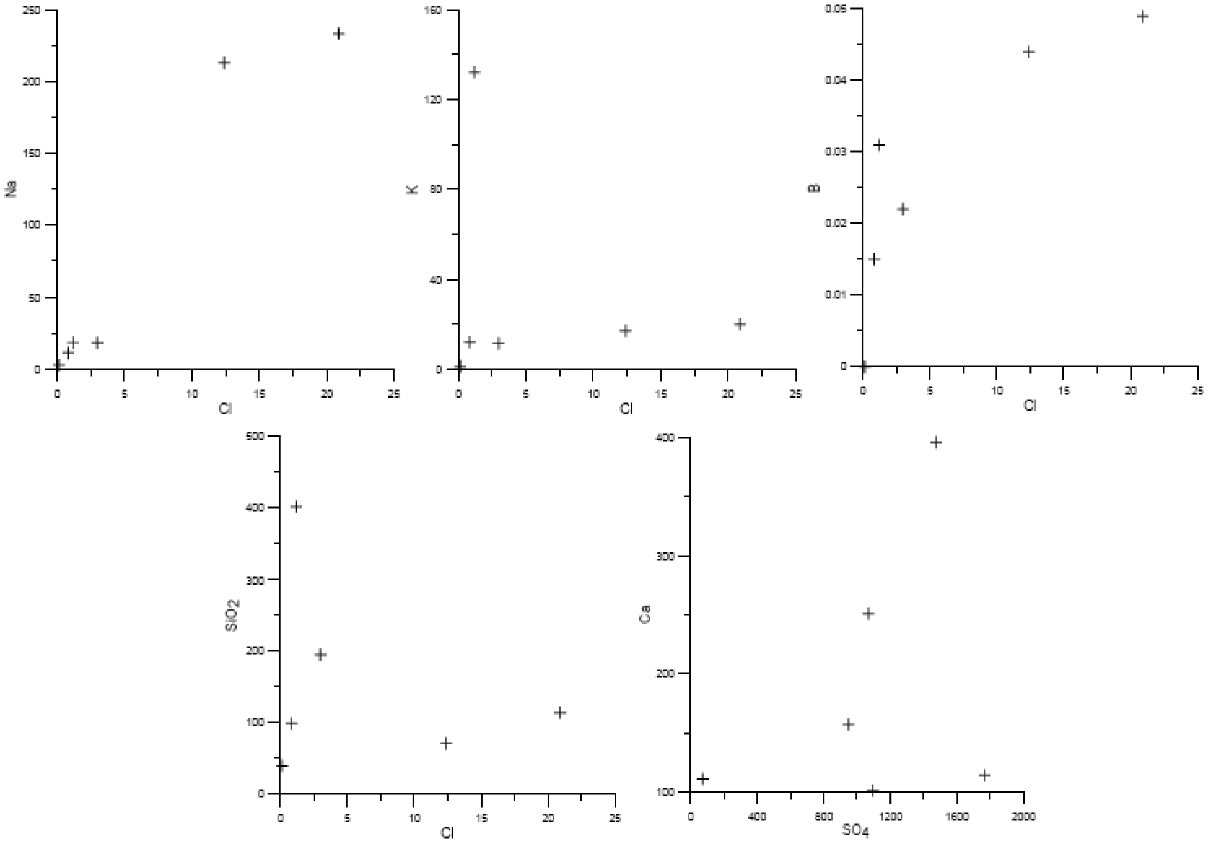

Figure 4. Binary plot of Cl vs. cations B and SiO_2 and SO_4 vs. Ca, units are in ppm.

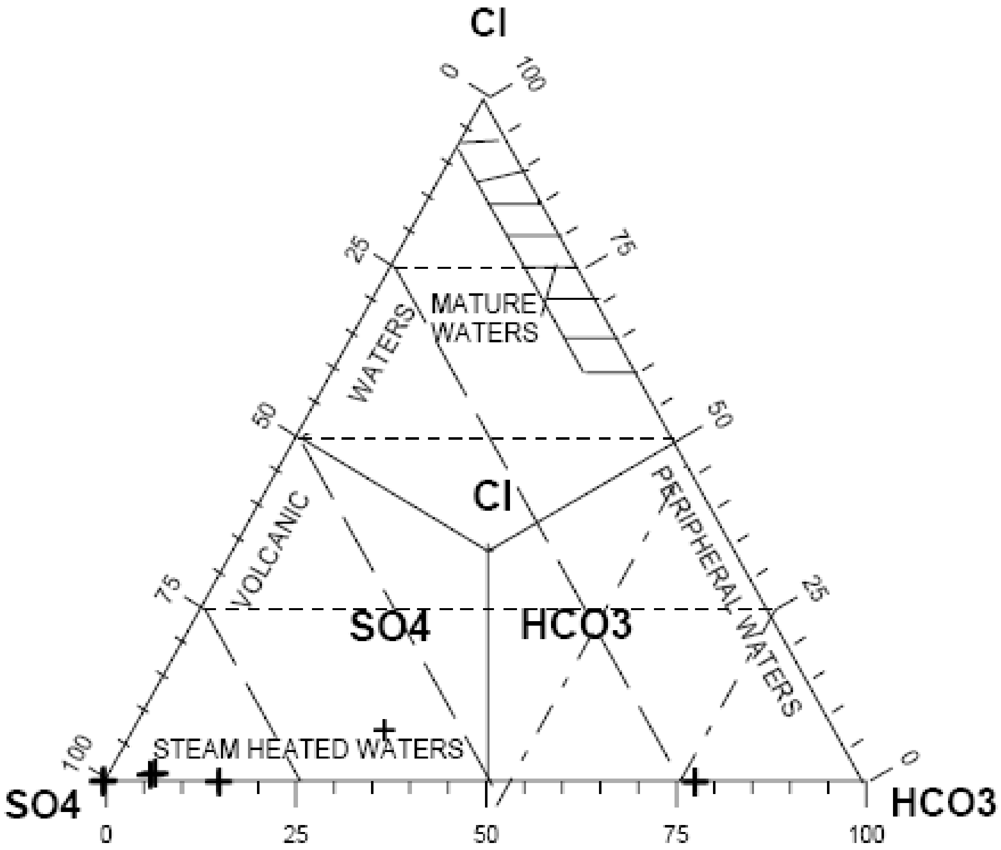

FIGURE 3: Cl-SO4-HCO3 ternary diagram for classification of Alid water waters

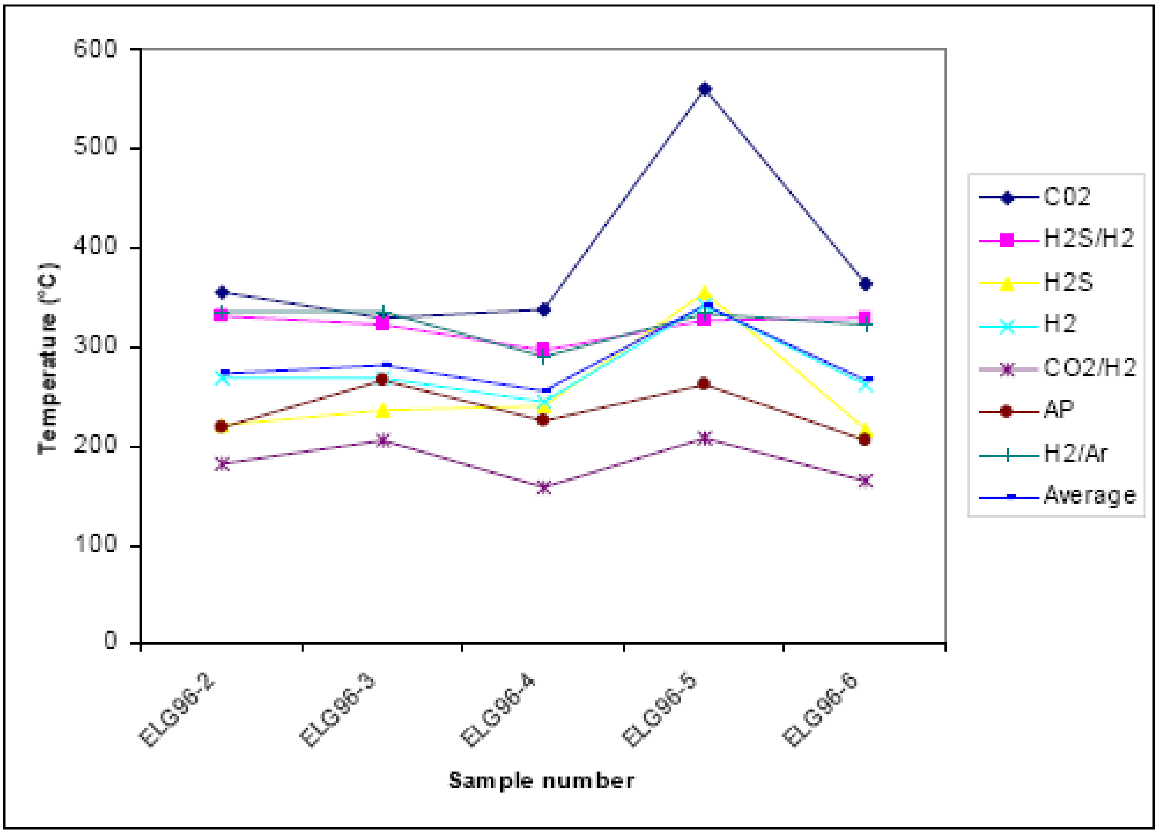

FIGURE 5: Scatter plot of gas geothermometers of Alid gassamples. The CO2, H2S, H2, and CO2/H2 are geothermometers from Arnórsson and Gunnlaugsson (1985); AP is D'Amore and Panichi(1980), and H2/Ar is the Giggenbach (1991) geothermometer

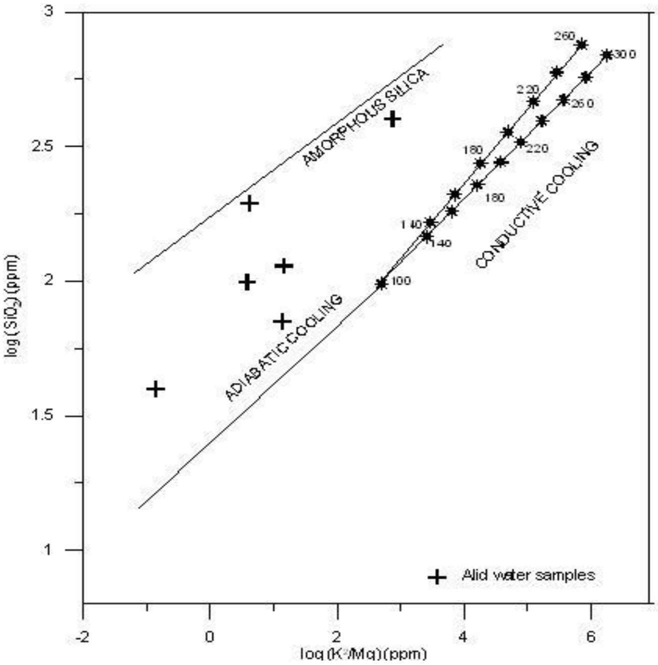

Figure 6: Alid gas samples plot showing log concentration of CO_2/Ar vs. H_2/Ar equilibrium diagram

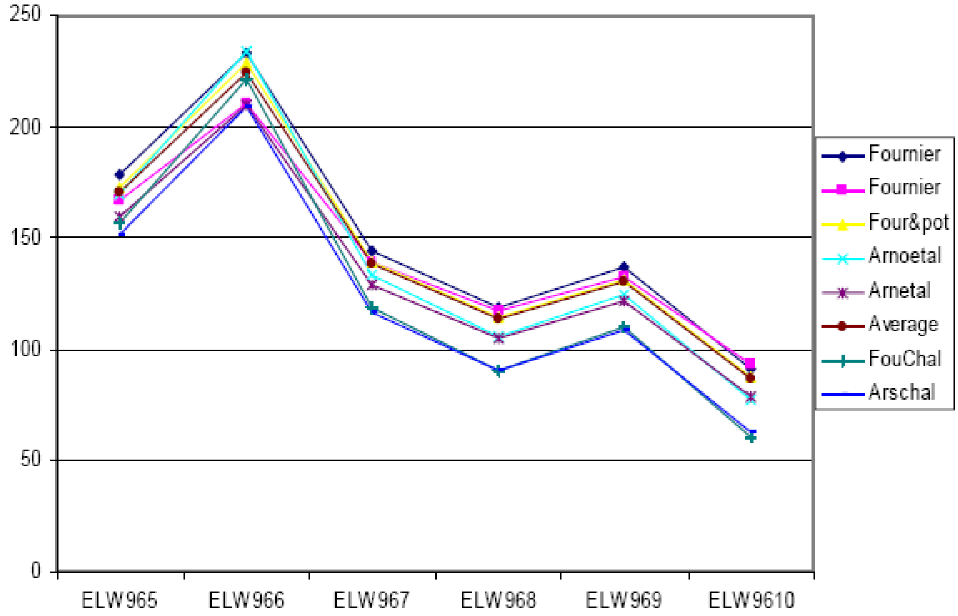

FIGURE 7: Calculated temperatures of Alid water samples with the response of the various silica geothermometers. The two Fourniers represent Equations 1 and 2, respectively, in Fournier (1977); Four & Pot is Fournier and Potter (1982); Arnoetal is Equation 5 in Arnórsson (2000); Arnetal is Equation 6 in Arnórsson (2000); FouChal is the Chalcedony equation - Equation 9 in Fournier (1977); and Arschal is Arnórsson et al. (1983)

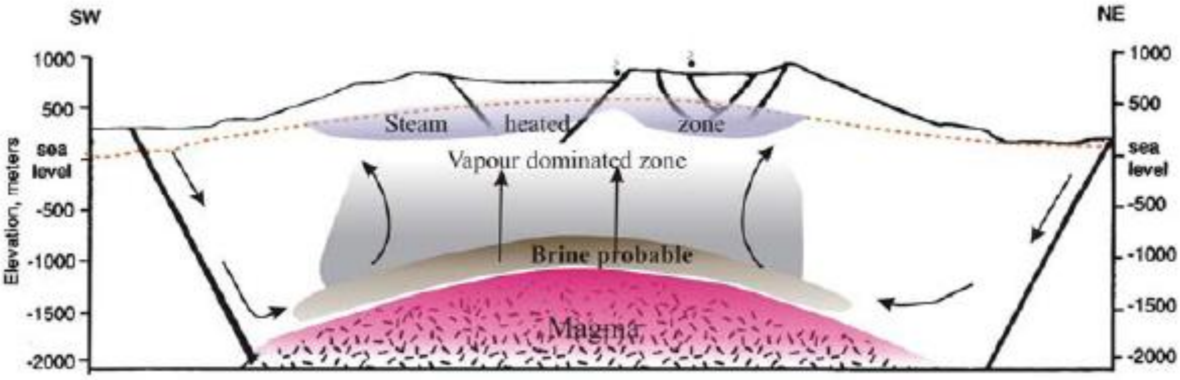

FIGURE 8: Conceptual model of Alid geothermal field based on geochemistry