

Geochemical Interpretation of Borehole Waters from Ambado-PK 20 area, Djibouti

Daher Ali Hassan and Idil Souleiman Bouraleh

Djiboutian Office for Geothermal Energy Development (ODDEG)

daherali12@hotmail.com ; idilsoule86@gmail.com

Keywords: Djibouti, Ambado-PK 20, borehole water, geothermometer.

ABSTRACT

The Ambado-Pk20 field is located in the centre of the Republic of Djibouti, this area is affected by faults and is dominated by several types of formations such as basaltic and rhyolite series. The area lacks surface manifestations, but the water wells have high temperatures. This geochemical study is focused on sampling and analysis (physico-chemical, trace elements and isotopes) of twenty-six boreholes in the PK 12, PK 20, Nagad, Doua, Damerjog and Ali Ouné sectors. The chemical characteristics of water wells in the Ambado-PK-20 study area are generally $\text{Cl-HCO}_3\text{-Na}$ type and are low mineralized at PK 20 but high mineralized at Nagad, Doua and Damerjog. The nature of the water wells may be from the groundwater (superficial water). The silica geothermometer and cation geothermometer give relatively wide temperature values. This can be explained by the fact that these water wells are immature and, therefore, classic geothermometers cannot be applied in this study. Thus, the reservoir temperature could not be estimated using those methods. The stable isotopic (δD and $\delta^{18}\text{O}$) composition and Cl/B ratio were used to determine the origin of the water. The water wells are meteoric waters from the superficial water, and they are not mixed with seawater. In order to improve this study, it is recommended to carry out temperature gradient or logging measurements in the boreholes and further analyses to estimate the reservoir temperature.

1. INTRODUCTION

The Republic of Djibouti has a 23,000 km^2 surface area and is located on the East Africa rift between Somalia and Ethiopia (Figure 1). Geologically, Djibouti is characterized by surface manifestations like volcanic rocks, faults, fumaroles, hot and warm springs etc.

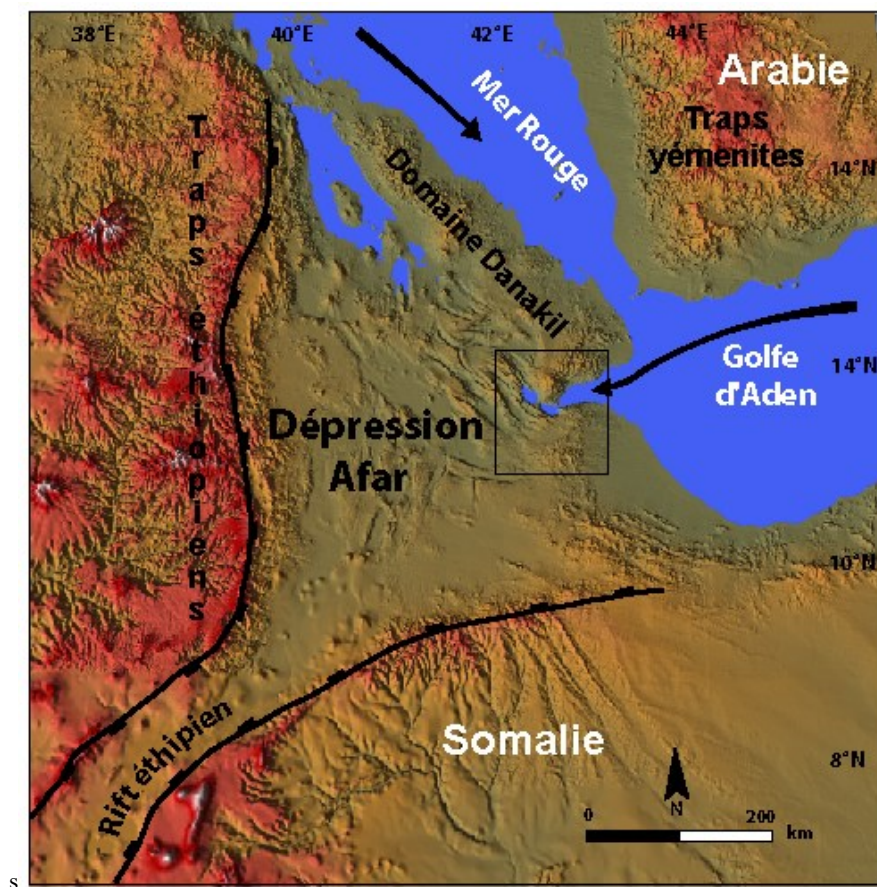


Figure 1: Numeric model (Gtopo30) of the Afar Triangle. The black square indicates the Republic of Djibouti.

The Ambado-PK 20 field (Figure 2) is located in the center of the Republic of Djibouti. This area has high tectonic activity related to the opening of the Gulf of Tadjourah. It is affected by dense fault networks mainly along the E-W direction that disappears to the east in the side of the Hayabley volcano, so the Hayabley volcano is posterior to the faults by covering the basalt of the gulf (marker of the opening of the Gulf of Tadjourah), and to the west these faults curve at the approach of Arta's relief bulge (Med Daoud et al.).

This geochemical study focused on sampling and analyses (physico-chemicals, trace elements and isotopes) of twenty-six boreholes waters in PK 12, PK 20, Nagad, Douda, Damerjog and Ali Ouné sectors. These samples were collected from January 30 to February 6, 2017. The purpose of this study is to determine the chemical composition of water from boreholes, to classify these waters and to determine their origin. On the other hand, the geothermometers were used to estimate the reservoir temperature.

This geochemical study will be composed as follows: first of all, the sampling methodologies and analytical protocols will be detailed and then the results and discussions of these analyses will be discussed.

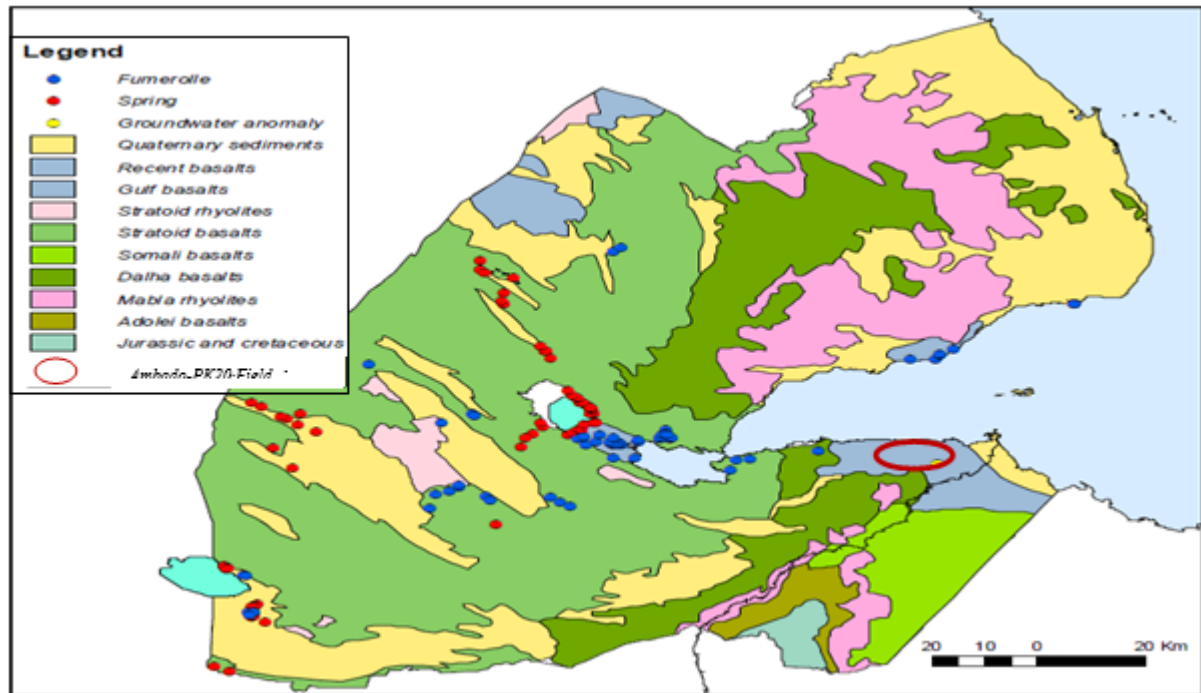


Figure 2: Djibouti, geology and geothermal surface manifestations (CERD).

2. METHODOLOGY

The geochemical study of the Ambado-PK20 site focused on sampling 26 boreholes (Figure 3). Some in-situ measurements were taken of the field such as: temperature measurements, pH, conductivity and verification or updating coordinates of the boreholes. These field parameters were measured using a pH-meter pH EUTECH instruments 610, conductivity EUTECH instruments COND610 and two electronic thermometers (Hanna Check Tempet Quick Fisher Scientific). The calibration of pH and EC are made earliest every day collection. Generally, the sample measurement was performed with a margin of error equal to $\pm 0.1^\circ\text{C}$ for the temperature, 1 s/cm for electrical conductivity and 0.01 units for pH.

The major cations and anions major concentrations were determined at the chemistry laboratory of CERD (center study research of Djibouti) by liquid chromatography (HPLC) using a Dionex TM ICS 3000 chromatograph. The carbonates (CO_3^{2-}) and the bicarbonates (HCO_3^-) were dosed by the method of Gran (by titration with HCl), by colorimetry with ammonium molybdate method for silica (SiO_2) and the boron (Br) was analyzed with ICP – AES HORIBA.



Figure 3: Locations of the boreholes in Ambado-PK-20 area.

Table 1: Results of physicochemical analyzes performed on samples of Ambado-PK20 water wells.

Nom	T(°C)	pH	EC (µS/cm)	TDS	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K(mg/l)	Li (mg/l)	NH ₄ (mg/l)	HCO ₃ (mg/l)	Cl (mg/l)	SO ₄ (mg/l)	NO ₃ (mg/l)	NO ₂ (mg/l)	F (mg/l)	Br (mg/l)	SiO ₂ (mg/l)	B (mg/l)	δ ¹⁸ O (‰)	δD (‰)	Charge balance
AWR 2	56,2	7,65	1236	843	43,62	34,77	164,21	8,05	0,29	0,16	289,45	184,73	71,37	44,74	0,05	0,51	0,82	94,59	0.332	-1.39	-3.1	4
PK 23	54,3	7,74	1440	957	32,45	35,24	218,98	7,22	0,05	0,08	285,00	226,65	111,56	38,66	0,01	0,42	0,90	67,30	0.467	-1.88	-5.2	3
FU 7	46,7	7,67	1504	952	49,33	47,29	181,18	9,42	0,06	0,01	237,55	262,07	105,48	58,33	0,02	0,56	1,02	92,73	0.465	-1.63	-4.7	3
Z 26	43,7	7,38	1637	1099	47,69	51,04	225,05	16,03	0,03	0,02	342,09	268,85	104,61	42,35	0,01	0,58	1,10	102,04	0.689	-	-	4
Z 28	43,1	7,66	1805	1099	42,32	56,60	223,34	14,63	0,02	0,02	326,62	304,93	95,90	33,46	0,01	0,53	1,12	96,14	0.62	-2.02	-7.2	3
EA 3	41,2	7,97	1704	976	40,79	46,99	207,76	8,75	0,17	0,05	185,80	330,33	103,27	50,81	0,02	0,37	1,23	66,37	0.501	-1.69	-5.5	2
WEA	37,3	7,46	1238	918	41,03	46,48	162,83	5,05	0,05	0,01	393,37	150,14	80,82	35,95	0,08	0,63	1,53	74,12	0.545	-1.56	-5.1	3
E 26	39,6	7,54	4258	2104	109,22	132,64	421,57	24,96	0,09	0,51	256,46	784,45	254,89	115,62	0,04	0,91	2,92	88,39	0.565	-1.84	-5.0	6
E 21	38,7	7,61	4418	2400	123,54	154,80	455,63	17,72	0,06	0,72	271,53	1160,33	172,29	39,11	0,09	0,72	3,94	91,49	0.507	-1.61	-4.5	-2
RG 5	42,7	7,54	4302	2328	122,76	143,45	492,89	16,20	0,10	0,38	204,00	1132,47	167,09	43,91	0,10	0,58	3,77	92,73	0.63	-1.75	-5.1	1
E 9 BIS	39,8	7,20	4572	2564	168,10	166,77	503,42	26,77	0,89	0,59	219,82	1217,96	211,73	43,87	0,10	0,49	3,87	109,17	0.697	-1.66	-4.1	3
E 16 BIS	38,8	7,34	4373	2409	130,00	118,98	554,93	24,22	0,65	0,55	231,39	1193,09	120,31	29,86	0,09	0,63	3,91	124,68	0.552	-1.95	-5.8	1
E 1	38,2	7,21	9310	5132	342,01	392,23	985,00	24,53	0,18	0,80	284,96	2622,47	410,79	59,80	0,13	0,43	8,27	94,90	0.921	-1.50	-3.7	3
H 2	40,1	7,54	5633	2949	139,74	214,00	649,14	12,05	0,08	0,47	134,33	1569,44	182,72	40,35	0,18	0,90	5,25	63,89	0.507	-1.58	-4.7	3
CCO	42,6	7,12	8852	4673	274,18	377,18	932,37	19,70	2,45	2,94	145,78	2626,09	218,45	64,16	0,33	0,94	7,99	72,88	0.65	-1.7	-4.0	3
RG2-BIS	41,8	7,0	7881	4231	281,30	352,67	792,50	22,98	0,37	0,67	171,09	2296,10	233,87	70,95	0,31	0,59	7,15	95,21	0.704	-1.52	-3.4	4
E 24	38,0	7,38	6617	3630	241,64	337,53	618,90	16,37	0,09	0,31	254,17	1911,47	209,39	32,00	0,42	1,31	6,45	104,83	0.46	-1.68	-4.5	4
PK 20-17	50,4	7,51	1455	943	28,11	34,27	222,94	6,04	0,43	0,19	285,80	229,73	89,55	44,12	0,05	0,58	1,03	68,85	0.522	-1.71	-4.4	4
FU 2 BIS	55,7	7,83	1298	923	31,09	31,34	201,52	5,27	0,05	≤ LD	345,31	193,19	77,47	36,59	0,03	0,53	0,78	58,62	0.424	-1.64	-4.1	1
FU 3	53,7	7,53	1248	845	27,51	32,62	192,24	4,95	0,02	0,01	295,00	181,65	70,91	38,79	0,01	0,56	0,68	76,30	0.413	-1.6	-3.8	5
E 30	45,2	7,45	2482	1448	78,40	52,99	353,81	18,09	0,21	0,12	232,89	557,37	116,45	35,31	0,06	0,50	1,87	111,96	0.467	-1.71	-5.1	5
E 3 BIS	39,7	7,0	13900	8378	710,41	779,56	1299,25	41,54	0,30	1,00	187,26	4563,66	714,10	66,20	0,58	1,16	13,33	82,81	1.035	-1.45	-4.0	3
FU 3 BIS	53,3	7,38	1538	931	50,67	33,41	195,36	9,57	0,20	0,04	227,07	257,67	88,28	67,27	0,07	0,63	1,01	91,18	0.489	-1.51	-3.6	4
EA 1	47,8	7,31	2030	1093	61,42	58,40	227,32	8,69	0,05	0,02	158,76	396,87	121,90	57,53	0,19	0,70	1,52	64,82	0.479	-1.71	-4.4	5
AWR 5	61,4	7,29	2043	1126	42,89	23,46	314,45	12,22	0,17	≤ LD	211,47	415,45	57,80	46,19	0,17	0,34	1,52	125,92	0.379	-1.74	-5.3	5
H 1	41,2	7,34	4387	2278	117,40	143,83	527,54	6,12	0,04	0,01	124,25	1169,60	138,03	47,09	0,16	0,56	3,69	63,27	0.473	-1.67	-4.4	4
Doraleh	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	-1.3	-1.1	-
Bouleh- Bivaleh	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	-1.2	-0.9	-

3. RESULTS AND DISCUSSION

The results of the analysis of twenty-six (26) samples from borehole waters in the Ambado-Pk20 area are presented in Table 1. The samples from the borehole waters of PK-20 area, PK-12 Dorale hare slightly mineralized with a conductivity between 1236 and 2482 $\mu\text{S}/\text{cm}$. On the other hand, in the Nagad, Douda and Damerjog zones, the samples are strongly mineralized with conductivities between 4300 and 13900. The pH values of these waters are between 7 and 7.9, which shows that these waters can be classified as neutral. The temperatures of the samples varied between 37.3-61.4°C (see Table 1).

3.1 Classification of the Samples

The Piper diagram (Piper, 1944) uses major elements to represent the different facies of groundwater. It allows a representation of anions and cations on two specific triangles whose sides show relative contents each of the major ions relative to the total of these ions (cations for the left triangle, anions for the right triangle). Figure 4 shows that the dominant anion in the analyzed waters is the chloride ion. This means that all waters are chlorinated. For cations, the dominant ion is Na-K. As a result, the waters can be attributed to sodium chloride and potassium facies.

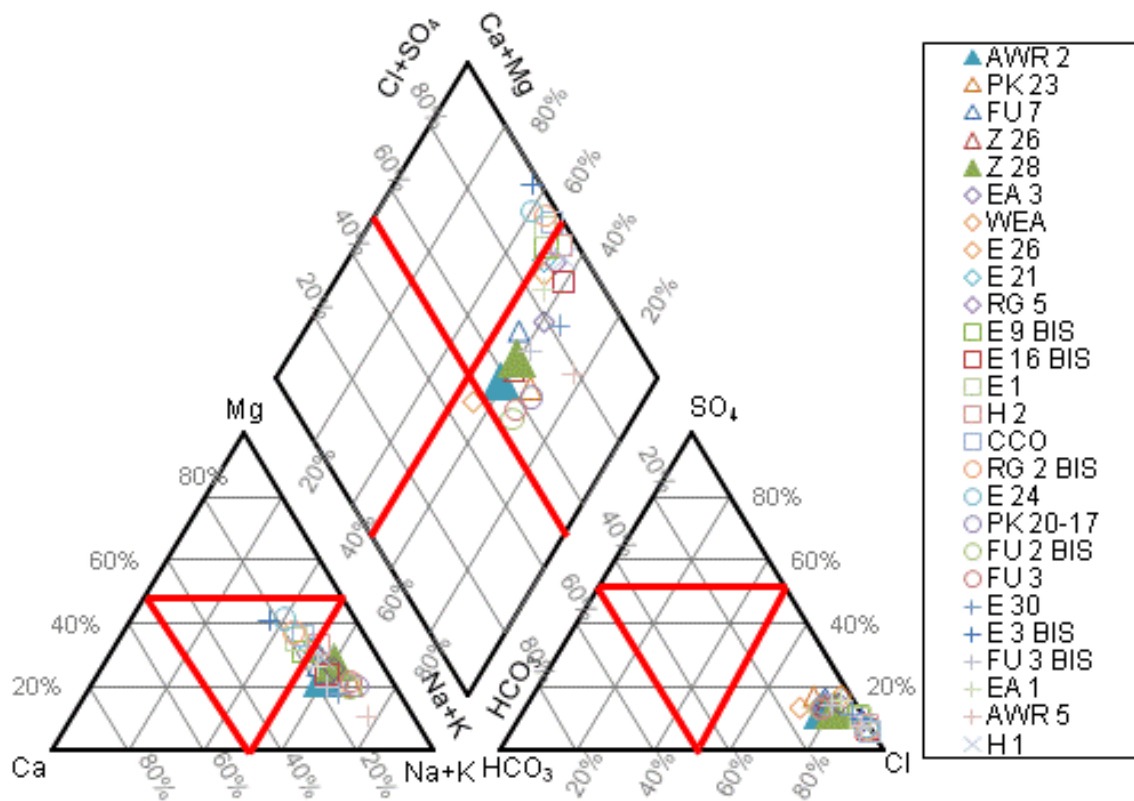


Figure 4: Piper diagram of Ambado-PK20 borehole water.

The ternary diagram $\text{Cl}-\text{SO}_4-\text{HCO}_3$ proposed by Giggenbach (1991) is used to distinguish different types of geothermal waters. The interpretation of the geothermal water chemistry is performed on the basis of an initial classification in terms of the major anions Cl, SO_4 and HCO_3 . The position of a data point in such a triangular diagram is obtained by first summing the concentrations of the three constituents involved. In the present case:

$$S = C_{\text{CL}} + C_{\text{SO}_4} + C_{\text{HCO}_3} \quad (1)$$

The next step is to calculate %Cl, % SO_4 and % HCO_3 using the following equations:

$$\% - \text{CL} = \frac{100C_{\text{CL}}}{S}; \% - \text{SO}_4 = \frac{100C_{\text{SO}_4}}{S}; \% - \text{HCO}_3 = \frac{100C_{\text{HCO}_3}}{S} \quad (2)$$

It appears from the $\text{Cl}-\text{SO}_4-\text{HCO}_3$ ternary diagram (Figure 5) that these waters are not mature waters and peripheral waters. In addition, these waters are located along the $\text{Cl}-\text{HCO}_3$ axis of the diagram. This means that these waters are Chlorinated-Bicarbonates.

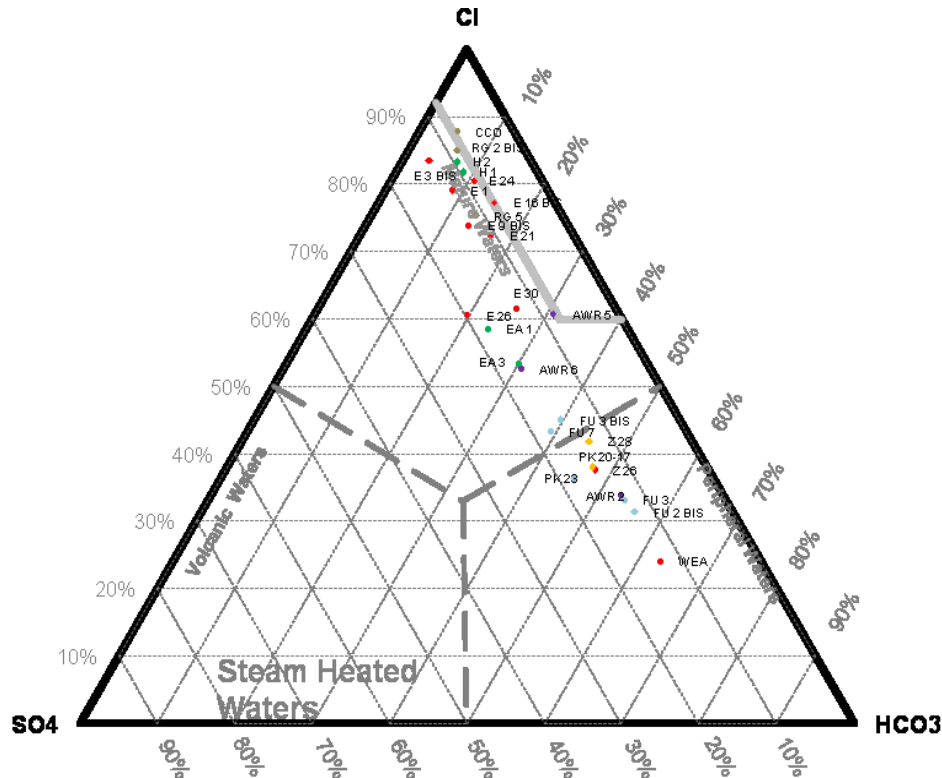


Figure 5: The CI-SO₄-HCO₃ ternary diagram of the borehole waters from the Ambado-PK20 area.

3.2 Solute Geothermometers

Applying geothermometry to analyze the chemical composition of the sampled waters enables estimating the temperature at which the waters were carried in the subsurface. In this study, most of the known chemical geothermometers were applied to the sampled waters from the Ambado-PK20 drilling. The results are reported in Table 2. The dissolved silica may be controlled either by chalcedony or by quartz. However, according Arnórsson (1975) and Michard (1990), basalt medium, silica dissolved is rather controlled by the quartz at temperatures above 150-170°C and chalcedony for temperatures below that limit.

Silica geothermometry (quartz and chalcedony) shows that the temperatures vary between 84-144°C while the cation geothermometry gives temperatures between 45-168°C (see Table 2). For these waters, geothermometers give a broad range of temperature values. This can be explained by the fact that these waters are immature and therefore classic geothermometers cannot be applied.

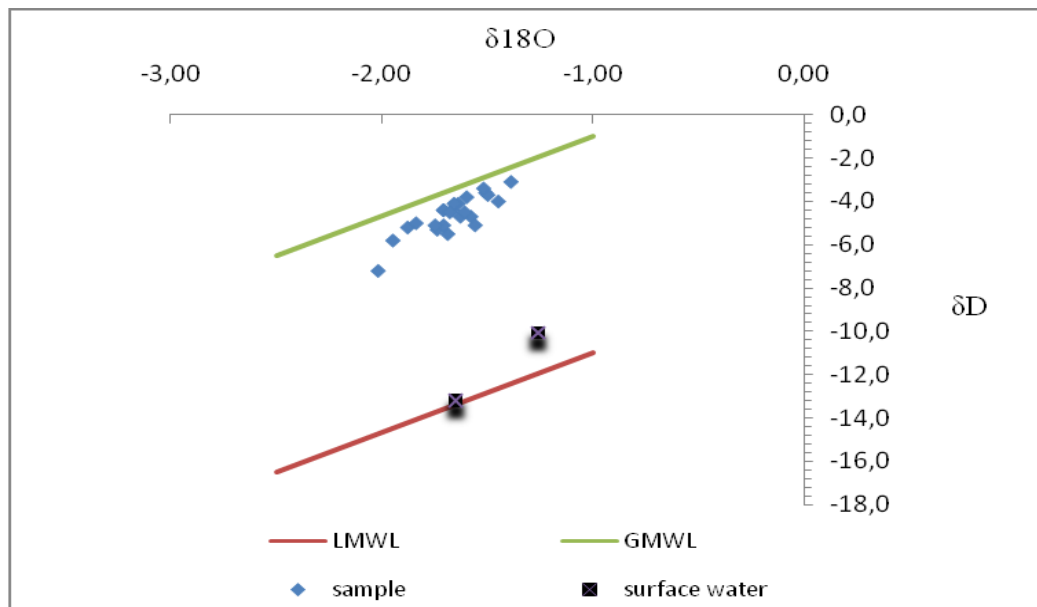
Table 2: Chemical geothermometers applied to borehole water at the Ambado-PK 20 site. T(°C)in this case.

Name	T _{Sample}	T _{QTZ}	T _{QTZ}	T _{calcédoine}	T _{calcédoine}	T _{Na-K (4)}	T _{Na-K}	T _{K-Mg}	T _{Na-K-Ca B=4/3}	T _{Na-K-Ca B=1/3}	T _{Na-Li (2)}
AWROLOFOUL 2	56,2	134	134	107	106	132	148	282	80	138	177
PK 23	54,3	116	116	87	88	104	124	284	86	127	88
FU 7	46,7	133	133	106	105	137	152	282	83	142	98
Z 26	43,7	138	138	112	110	163	174	273	106	160	63
Z 28	43,1	135	135	108	107	155	168	275	105	157	56
EA 3	41,2	116	116	87	87	121	138	283	87	136	138
WEA 10	37,3	121	121	93	93	100	121	294	66	119	97
E 26	39,6	130	131	103	102	147	160	273	110	155	84
E 21	38,7	132	132	105	104	115	134	281	95	136	66
RG 5	42,7	133	133	106	105	104	124	282	93	129	82
E 9 BIS	39,8	142	142	116	114	138	153	274	103	149	177
E 16 BIS	38,8	150	150	125	122	123	141	273	107	143	155
E 1	38,2	134	134	107	106	86	110	284	91	120	79
H 2	40,1	114	114	85	85	69	96	292	83	109	66
CCO	42,6	120	120	92	92	77	102	288	88	114	200
RG 2 BIS	41,8	134	135	107	106	96	117	284	91	125	114
E 24	38,0	140	140	113	112	90	113	290	80	119	69
PK 20-17	50,4	117	118	89	89	91	114	287	83	121	182
FU 2 BIS	55,7	109	110	80	81	89	112	289	76	117	87
FU 3	53,7	123	123	94	94	88	111	291	76	117	64
E 30	45,2	144	144	118	116	135	150	271	103	148	123
E 3 BIS	39,7	127	127	99	99	102	123	280	96	130	87
FU 3 BIS	53,3	132	132	105	104	132	148	278	84	140	148
EA 1	47,8	114	115	85	86	114	133	285	78	130	83
AWROLOFOUL 5	61,4	150	151	125	123	115	134	271	102	138	121
H 1	41,2	113	113	84	85	45	76	302	63	90	55

3.3 Origin of Waters

3.3.1 Isotopes

In the study area, oxygen and hydrogen isotopes are plotted and compared to the global meteoric line (GMWL) and the local meteoric line (LMWL). Equations for GMWL defined by Craig (1961) and LMWL defined by Fontes et al. (1980) are respectively: $Dd = 8 * d18O + 10$ and $Dd = 8 + 0 * d18O$.

**Figure 6: Isotopic composition of the borehole water at the Ambado-PK20 site.**

The analysis of stable isotopes, deuterium and oxygen-18, drilling water showed that experimental points of the study area is placed very close to the right of the GMWL. Therefore, these waters (Figure 6) are of meteoric origin and they contribute in major part to their charge. Likewise, the surface waters are close to the right of the LMWL. This can be explained from the fact that surface water does not come from the same source of water because of the shift Dd is superior than 4%.

3.3.2 δD /Cl Ratio

Deuterium diagram chloride function show as whether water drilling are mixed with seawater. On the one hand, the low concentration of chloride (see Table 1) of this drilling water shows that there is no infiltration of seawater. On the other hand, Figure 7 below shows that these waters are far away from the mixing line. Hence these waters drilling is not mixed with seawater.

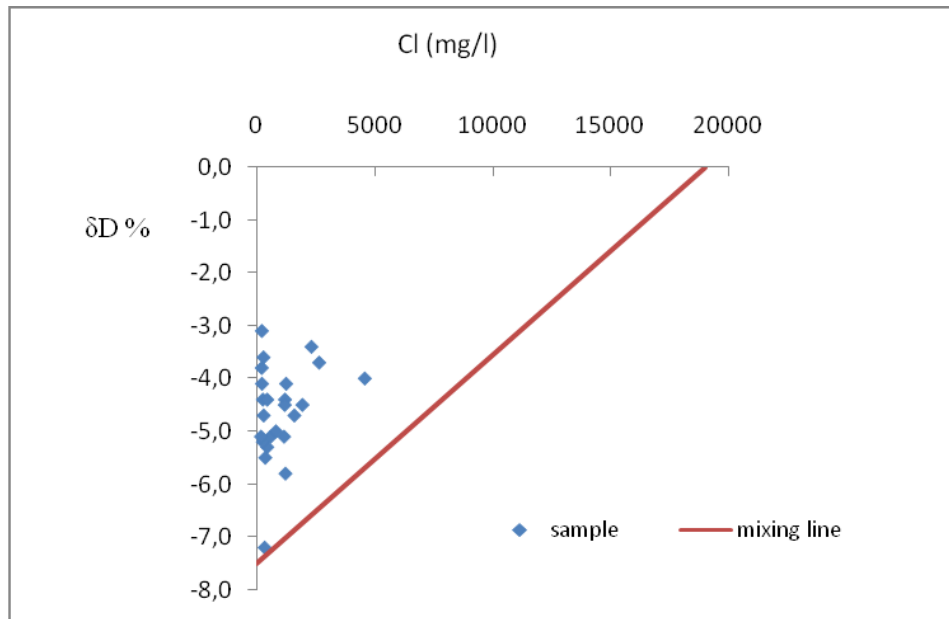


Figure 7: δD vs Cl diagram of boreholes water at the Ambado-PK20 site

3.3.3 Cl/B Ratio

The report in B and C geothermal water was used to obtain information on the origin of these waters (White, 1957a,b; White et al., 1963; Truesdell, 1976) to assess the mixture of hot water and cold water in the areas of geothermal systems and evaluate other characteristics of these systems (Ellis, 1970; White, 1970; Fournier, 1977, 1979; Arnórsson 1985; Janik et al, 1991; Truesdell, 1991).

The concentration of chloride and boron rainwater and groundwater is generally much lower than geothermal fluid. Figure 8 shows that water in this area is far from being seawater and concentrations of these two components (Cl and B) are low in these waters (Ambado PK-20). As a result, the water sampled from Ambado PK-20 can be groundwater.

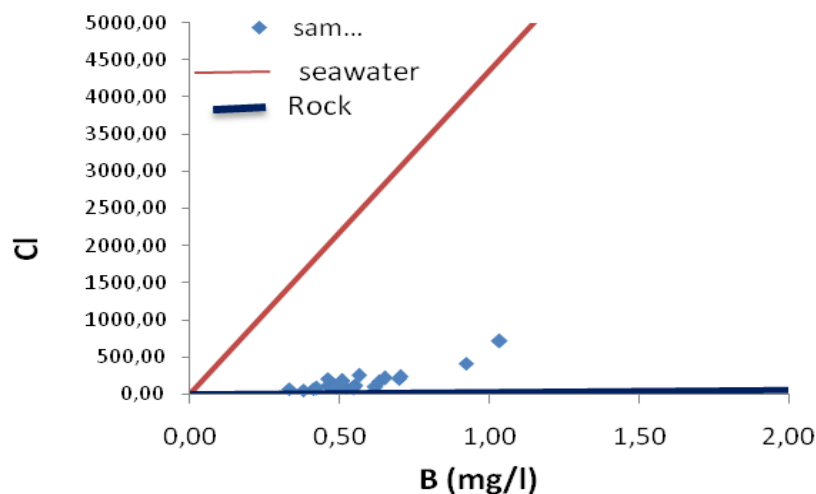


Figure 8: δD vs Cl-diagram of water at the Ambado-PK20 site.

4. CONCLUSIONS AND RECOMMENDATION

In this pre-feasibility study, twenty-six drill holes were analyzed to estimate reservoir temperatures and to determine the origin of water at sampled wells. The chemical characteristics of the water from the Ambado-PK-20 study area are usually chlorinated-sodium bicarbonate-types, and are low mineralized in PK 20 and strong mineralized for Nagad, Douda and

Damerjog. These waters can be a result of a small infiltration of seawater. The waters of these wells can be groundwater (groundwater of Djibouti). These waters are immature and are not balanced with the rocks of the reservoir; therefore, the calculations of classical geothermometry are not applicable to estimate the reservoir temperature. To do this, it is suggested that temperature gradient or logging measurements should be carried out in the boreholes, as well as additional analyses such as isotopic analysis (sulfur 34, oxygen 18 and sulfates) may help to give estimates of the reservoir temperature.

REFERENCES

- Arnórsson S., 1975: Application of the silica geothermometer in low temperature hydrothermal areas in Iceland. *Amer. J. Sci.*, 275, 763-784.
- Arnórsson, S., Sigurdsson, S. and Svavarsson, H., 1982: The chemistry of geothermal waters in Iceland I. Calculation of aqueous speciation from 0°C to 370°C. *Geochim. Cosmochim. Acta*, 46, 1513-1532.
- Arnórsson, S., and Svavarsson, H., 1985: Application of chemical geothermometry to geothermal exploration and development. *Geoth. Res. Council, Transactions*, 9-1, 293-298.
- Craig, H., 1961: Isotopic variations in meteoric water. *Science*, 133, 1702-1703.
- Ellis, A.J., 1970: Quantitative interpretation of chemical characteristics of hydrothermal systems. *Geothermics*, 2, 516-527.
- Fournier, R.O., 1977: Chemical geothermometers and mixing model for geothermal systems. *Geothermics*, 5, 41-50.
- Fournier, R.O., and Potter, R.W. II, 1979: Magnesium correction to the Na-K-Cageothermometer. *Geochim. Cosmochim. Acta*, 43, 1543-1550.
- Fournier, R.O., 1990: The interpretation of Na-K-Mg relations in geothermal waters. *Geothermal Resources Council, Transactions* 14, 1421-1425.
- Giggenbach, W.F., 1988: Geothermal solute equilibria. Derivation of Na-K-Mg-Cageoindicators. *Geochim. Cosmochim. Acta*, 52, 2749-2765.
- Giggenbach, W.F., 1991: Chemical techniques in geothermal exploration. In: D'Amore, F. (coordinator), *Application of geochemistry in geothermal reservoir development*. UNITAR/UNDP publication, Rome, 119-144.
- Michard G., 1990: Behaviour of major elements and some trace elements (Li, Rb, Cs, Fe, Mn, W, F) in deep hot waters from granitic areas. *Chem. Geol.* 89, p. 117-134.
- Piper, A.M. (1944). A graphic procedure in the geochemical interpretation of water-analyses. *Transactions of the American Geophysical Union* 25, 914-923.
- Reed, M.H., and Spycher, N.F., 1984: Calculation of pH and mineral equilibria in hydrothermal water with application to geothermometry and studies of boiling and dilution. *Geochim. Cosmochim. Acta*, 48, 1479-1490.
- Truesdell, A.H., 1976: Summary of section III - geochemical techniques in exploration. *Proceedings of the 2nd U.N. Symposium on the Development and Use of Geothermal Resources*, San Francisco, 1, liii-lxxix.
- Truesdell, A.H., 1991: Effects of physical processes on geothermal fluids. In: D'Amore, F. (coordinator), *Application of geochemistry in geothermal reservoir development*. UNITAR/UNDP publication, Rome, 71-92.
- White, D.E., Hem, J.D., and Waring, G.A., 1963: Chemical composition of sub-surface waters. In: Fleischer, M. (ed.), *Data of Geochemistry* (6th ed.), US Geol. Survey, Prof. Paper 440F.
- White, D.E., 1970: Geochemistry applied to the discovery, evaluation, and exploration of geothermal energy resources. *Geothermics*, Sp. issue, 2-1, 58-80.