Geochemical and Isotopic Interpretation of Boreholes Waters from Ambado-PK 20 area, Djibouti.

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ABSTRACT

The Ambado-Pk20 area, Djibouti, is affected by faults and dominates by several types of formation such as the basaltic and rhyolite series. In this area, there are not surface manifestations but the water wells have high temperatures. The purpose of this study is to determine the chemical composition of twenty six borehole waters in PK 12, PK 20, Nagad, Douda, Damerjog and Ali Ouné sectors, to classify these waters, to estimate the reservoir temperature and to determine their origin. The chemical characteristics of water wells in the Ambado-PK-20 study area are generally Cl-HCO₃-Na type and are low mineralized at PK 20 but high mineralized at Nagad, Douda and Damerjog. The nature of the water wells may be from the groundwater (superficial water). According to ternary diagram (Na-K-Mg), these waters are not equilibrated with the reservoir rocks. 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 cannot be estimated. The stable isotopic (δD and δ^{18} 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 the sea water. In order to improve this study, it is recommended to make a temperature gradient or logging of the boreholes and also to do additional analyses to estimate the reservoir temperature.

1. Introduction

The Republic of Djibouti is located on the East Africa rift between Somalia and Ethiopia with 23,000 km² surface area. Geologically, Djibouti is characterized by surface manifestations like volcanic rocks, faults, fumaroles, hot and warm springs etc...

The Ambado-PK 20 field (Figure 1) is located in the center of the Republic of Djibouti. This area is very active by the tectonic activities related to the opening of the Gulf of Tadjourah. It is affected by dense faults networks mainly E-W direction that disappears to the east in the side of 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.).



FIGURE 1: Djibouti, geology and geothermal surface manifestations (Jalludin, 2009)

This geochemical study focused on sampling and analyses of twenty six boreholes waters in PK 12, PK 20, Nagad, Douda, Damerjog and Ali Ouné sectors. These boreholes waters, from 180 to 200 m depth, were drilled by ONEAD (National Office for Water and Sanitation of Djibouti) for drinking to local people. These wells are closed and the waters were collected on the surface using the pump.

The samples were collected from January 30 to February 6, 2017. The purpose of this study is to determine the chemical composition of 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 analyzes will be discussed.

2. Methodology

This geochemical study focused on the results of 26 boreholes samples from the Ambado-PK20 site (Figure2). Some measurements were taken in-situ such as: temperature, pH, conductivity and verification or updating coordinates of these boreholes waters. These field parameters were measured with pH-meter (pH EUTECH instruments 610), conductivity meter (EUTECH instruments COND610) and two electronic thermometers (Hanna Check Tempet Quick Fisher Scientific). The calibration of pH and EC are made daily before collection. Generally, the sample measurement was performed with a margin of error equal to ± 0.1 ° C for the temperature, 1 s / cm for conductivity Electrical and 0.01 units for pH.



FIGURE 2: Location of water boreholes of Ambado-PK20 site.

The major cations (Ca²⁺, Mg²⁺, Na⁺, K⁺ and Li⁺) and major anions concentrations (Cl⁻, SO₄²⁻, NO³⁻, F⁻ and Br⁻) were determined in the chemistry laboratory of CERD (Center for Studies and Research of Djibouti) by liquid chromatographic (HPLC) using a Dionex TM ICS 3000 chromatograph. The carbonates (CO₃²⁻) and the bicarbonates (HCO₃⁻) were determined by the Gran titration method. Silica (SiO₂) was determined by colorimetric method using ammonium molybdate. And the boron (Br) was analyzed with ICP – AES HORIBA.

Nom	T(°C)	рН	EC (µS/cm)	TDS	Са	Mg	Na	K	Li	NH4	HCO ₃
AWR 2	56,2	7,65	1236	843	43,62	34,77	164,21	8,05	0,29	0,16	289,45
РК 23	54,3	7,74	1440	957	32,45	35,24	218,98	7,22	0,05	0,08	285,00
FU 7	46,7	7.67	1504	952	49,33	47,29	181,18	9,42	0,06	0,01	237,55
Z 26	43,7	7.38	1637	1099	47,69	51,04	225,05	16,03	0,03	0,02	342,09
Z 28	43,1	7,66	1805	1099	42,32	56,60	223,34	14,63	0,02	0,02	326,62
EA 3	41,2	7,97	1704	976	40,79	46,99	207,76	8,75	0,17	0,05	185,80
WEA	37,3	7,46	1238	918	41,03	46,48	162,83	5,05	0,05	0,01	393,37
E 26	39,6	7,54	4258	2104	109,22	132,64	421,57	24,96	0,09	0,51	256,46
E 21	38,7	7,61	4418	2400	123,54	154,80	455,63	17,72	0,06	0,72	271,53
RG 5	42,7	7,54	4302	2328	122,76	143,45	492,89	16,20	0,10	0,38	204,00
E 9 BIS	39,8	7,20	4572	2564	168,10	166,77	503,42	26,77	0,89	0,59	219,82
E 16 BIS	38,8	7,34	4373	2409	130,00	118,98	554,93	24,22	0,65	0,55	231,39
E 1	38,2	7,21	9310	5132	342,01	392,23	985,00	24,53	0,18	0,80	284,96
Н 2	40,1	7,54	5633	2949	139,74	214,00	649,14	12,05	0,08	0,47	134,33
ссо	42,6	7,12	8852	4673	274,18	377,18	932,37	19,70	2,45	2,94	145,78
RG2-BIS	41,8	7,0	7881	4231	281,30	352,67	792,50	22,98	0,37	0,67	171,09
E 24	38,0	7,38	6617	3630	241,64	337,53	618,90	16,37	0,09	0,31	254,17
РК 20-17	50,4	7,51	1455	943	28,11	34,27	222,94	6,04	0,43	0,19	285,80
FU 2 BIS	55,7	7,83	1298	923	31,09	31,34	201,52	5,27	0,05	≤LD	345,31
FU 3	53,7	7,53	1248	845	27,51	32,62	192,24	4,95	0,02	0,01	295,00
E 30	45,2	7,45	2482	1448	78,40	52,99	353,81	18,09	0,21	0,12	232,89
E 3 BIS	39,7	7,0	13900	8378	710,41	779,56	1299,25	41,54	0,30	1,00	187,26
FU 3 BIS	53,3	7,38	1538	931	50,67	33,41	195,36	9,57	0,20	0,04	227,07
EA 1	47,8	7,31	2030	1093	61,42	58,40	227,32	8,69	0,05	0,02	158,76
AWR 5	61,4	7,29	2043	1126	42,89	23,46	314,45	12,22	0,17	≤LD	211,47
H 1	41,2	7,34	4387	2278	117,40	143,83	527,54	6,12	0,04	0,01	124,25
Doraleh	-	_	_	_	_	_	_	_	_	_	_
Bouleh-Biyaleh	-	_	_	_	_	-	_	_	_	_	_

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

Nom	Cl	SO ₄	NO ₃	NO ₂	F	Br	SiO ₂	В	δ ¹⁸ Ο	δD	Balance ionique
AWR 2	184,73	71,37	44,74	0,05	0,51	0,82	94,59	0.332	-1.39	-3.1	4
РК 23	226,65	111,56	38,66	0,01	0,42	0,90	67,30	0.467	-1.88	-5.2	3
FU 7	262,07	105,48	58,33	0,02	0,56	1,02	92,73	0.465	-1.63	-4.7	3
Z 26	268,85	104,61	42,35	0,01	0,58	1,10	102,04	0.689	-	-	4
Z 28	304,93	95,90	33,46	0,01	0,53	1,12	96,14	0.62	-2.02	-7.2	3
EA 3	330,33	103,27	50,81	0,02	0,37	1,23	66,37	0.501	-1.69	-5.5	2
WEA	150,14	80,82	35,95	0,08	0,63	1,53	74,12	0.545	-1.56	-5.1	3
E 26	784,45	254,89	115,62	0,04	0,91	2,92	88,39	0.565	-1.84	-5.0	6
E 21	1160,33	172,29	39,11	0,09	0,72	3,94	91,49	0.507	-1.61	-4.5	-2
RG 5	1132,47	167,09	43,91	0,10	0,58	3,77	92,73	0.63	-1.75	-5.1	1
E 9 BIS	1217,96	211,73	43,87	0,10	0,49	3,87	109,17	0.697	-1.66	-4.1	3
E 16 BIS	1193,09	120,31	29,86	0,09	0,63	3,91	124,68	0.552	-1.95	-5.8	1
E 1	2622,47	410,79	59,80	0,13	0,43	8,27	94,90	0.921	-1.50	-3.7	3
Н 2	1569,44	182,72	40,35	0,18	0,90	5,25	63,89	0.507	-1.58	-4.7	3
ссо	2626,09	218,45	64,16	0,33	0,94	7,99	72,88	0.65	-1.7	-4.0	3
RG2-BIS	2296,10	233,87	70,95	0,31	0,59	7,15	95,21	0.704	-1.52	-3.4	4
E 24	1911,47	209,39	32,00	0,42	1,31	6,45	104,83	0.46	-1.68	-4.5	4
РК 20-17	229,73	89,55	44,12	0,05	0,58	1,03	68,85	0.522	-1.71	-4.4	4
FU 2 BIS	193,19	77,47	36,59	0,03	0,53	0,78	58,62	0.424	-1.64	-4.1	1
FU 3	181,65	70,91	38,79	0,01	0,56	0,68	76,30	0.413	-1.6	-3.8	5
E 30	557,37	116,45	35,31	0,06	0,50	1,87	111,96	0.467	-1.71	-5.1	5
E 3 BIS	4563,66	714,10	66,20	0,58	1,16	13,33	82,81	1.035	-1.45	-4.0	3
FU 3 BIS	257,67	88,28	67,27	0,07	0,63	1,01	91,18	0.489	-1.51	-3.6	4
EA 1	396,87	121,90	57,53	0,19	0,70	1,52	64,82	0.479	-1.71	-4.4	5
AWR 5	415,45	57,80	46,19	0,17	0,34	1,52	125,92	0.379	-1.74	-5.3	5
H 1	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-Biyaleh	_	_	_	_	—	—	—	—	-1.2	-0.9	-

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

3. Results and discussion

The results of the analysis twenty-six (26) samples from boreholes waters in the Ambado-Pk20 area are presented in Table 1. The samples from the boreholes waters of PK-20 area, PK-12 Dorale hare slightly mineralized with conductivity between 1236 and 2482 μ S / cm. On the other hand, in 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 show that these waters are neither basic nor acidic. The temperature of samples varies between 37.3-61.4 ° C (Table 1).

3.1 Classification of the samples

3.1.1 Piper diagram

The piper diagram (Piper, 1944) uses the 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 3 shows that the dominant anion in the analyzed waters is the chloride ion. This means that all waters are all chlorinated. In cations, the dominant ion is Na-K.As a result, the waters can be attributed to sodium chloride and potassium facies.



FIGURE 3: Piper diagram of Ambado-PK20 boreholes water

3.1.2The Cl-SO₄-HCO₃ Ternary diagram

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The ternary diagram $Cl-SO_4$ -HCO₃ proposed by Giggenbach (1991) is used to distinguish different types of geothermal waters. The interpretation of geothermal water chemistry is performed on the basis on an initial classification in terms of major anions Cl, SO4 and HCO3. 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:

$$S = C_{CL} + C_{SO_4} + C_{HCO_3}$$

The next step is to calculate %-Cl, %-SO4and %-HCO3by following equations:

$$\% - CL = \frac{100C_{CL}}{S}; \% - SO_4 = \frac{100C_{SO_4}}{S}; \% - HCO_3 = \frac{100C_{HCO_3}}{S}$$
$$\% - SO4 = \frac{100 Cso4}{S}$$

It appears from this diagram (Figure 4) these waters are located along the Cl - HCO3 axis of the diagram. This means that these waters are Chlorinated-Bicarbonates.



FIGURE 4: The Cl-SO4-HCO3 ternary diagram of the boreholes waters from Ambado-PK20 area.

FIGURE 5: Classification of the boreholes waters using the Na-K-Mg ternary diagram.

3.1.3 The Na-K-M ternary diagram

By Giggenbach (1988), the Na-K-Mg ternary diagram is used to classify the geothermal waters into three categories: fully mature, partially mature and immature. It is also used to estimate the reservoir temperature to select the suitable water use the previous figure 4. Figure 5 indicates that all of the Ambado-PK-20 borehole waters are located in the "immature waters" zone, out of complete equilibrium with the rock and close to the magnesium pole.

Which is not an index of high temperature in depth. Often, these properties characterize carbon-dioxide waters and result in a significant discrepancy between the results of different chemical geothermometers. The immature water indicates the initial dissolution of the minerals before the equilibrium reaction begins (Fourrier, 1990) or might be due to a high magnesium concentration, suggesting a high proportion of cold groundwater.

3.2 Solute Geothermometers

Name	TSample	Tqtz	Tqtz	Tcalcédoine	Tcalcédoine	T _{Na-K (4)}	T _{Na-K}	TK-Mg	T _{Na-K-Ca} B=4/3	T _{Na-K-Ca} B=1/3	T _{Na-Li} (1)
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
H1	41,2	113	113	84	85	45	76	302	63	90	55

 TABLE 2: Chemical geothermometers applied to boreholes water at the Ambado-PK 20 site.

Methods geothermometry chemical allow, from the water analysis, calculate the temperature at which they were carried in the under - ground " in their deposit". In this study, most of the known chemical geothermometers was applied to waters Ambado-PK20 drilling. The results were reported in Table 2. The dissolved silica may be controlled either by chalcedony or by quartz.

However, according Arnorsson (1975) and Michard (1990), basalt medium, silica dissolved is rather controlled by the quartz at temperatures above 150-170 $^{\circ}$ C and the chalcedony for temperatures below this limit.

Silica geothermometry (quartz and chalcedony) shows that the temperatures vary between 84-144 $^{\circ}$ C while the cation geothermometry gives temperatures between 45-168 $^{\circ}$ C (Table

2). For these waters, geothermometers give temperature values relatively broad. This can be explained by the fact that these waters are immature and therefore classic geothermometers cannot be applied in this case.

3.3 Origin of waters

3.3.1 Isotopes

In the study area, oxygen and hydrogen isotopes are plotted and compared to the line Global meteoric (GMWL) and local meteoric line (LMWL). Equations GMWL defined Craig (1961) and LMWL defined by Fontes et al. (1980) are respectively: $\delta d = 8 * \delta 180 + 10$ and $\delta d = 8 + 0 * \delta 180$.



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

The stable isotopic analyses of borehole waters showed that these waters are placed very close to the GMWL line (Figure 6). By Therefore, these waters are probably from meteoric water and they contribute in major part to their charge. As against the surface waters are close to the LMWL line. These surface waters come from different source than the borehole waters because the shift δD is superior than 4%.

3.3.2 δD /Cl Ratio

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



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

3.3.3 Cl / B Ratio



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

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; Arnorsson 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 drilling in this area are far from the sea water right and concentrations of these two components (Cl and B) are low in these waters (Ambado PK-20). As a result, water Ambado PK-20 drilling can be groundwater.

4. CONCLUSIONS AND RECOMMENDATION

In this pre-feasibility study, twenty six drill holes were analyzed to estimate of the reservoir temperature and to determine the origin of the drilling water. The chemical characteristic the boreholes water of Ambado-PK-20 study area are usually chlorinated-sodium bicarbonates-type and are low mineralized in PK 20 and strong mineralized to Nagad, Douda and Damerjog. These can come from a low infiltration of sea water in these drilling water. 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 to conduct the study of the gradient temperature or logging of boreholes, as well as additional analyzes such as isotopic analysis (sulfur 34, oxygen 18 and sulfates) may to give the estimate of reservoir temperature.

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