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Geochemical Study of Arta Geothermal field, Djibouti

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ABSTRACT

Arta is located in the east of the Republic of Djibouti. Located at an altitude of 750 m, on a mountain overlooking the Gulf of Tadjourah, the atmospheric temperature can drop to 10°C. The study of the Arta area involved sampling for six springs and seven water wells (dug wells) as well as three fumaroles. The region of Arta is considered as one of geothermal site the most estimated by the Republic of Djibouti. The flush volcanic trainings (formations) are: Rhyolites of Ribta, Rhyolites of Mabla, Basalt of Dalha, series stratoid of the Afar and Basalts of the gulf. The waters of Arta region springs and wells had neutral pH values. The temperature of the waters varied from 29.0°C to 39.0°C.

The general nature of spring waters is chloride-sulfate type whereas waters from water wells vary in chloride and bicarbonate contents. Boudadh, Qiqle, Bolleh, and Qof are rich in sodium and potassium of cation. Two water wells Boudadh and Qiqle are possibly partially equilibrated with rock, or affected by mixing of seawater. The other samples are considered immature water. The fumaroles of Arta area are very weak that the gases were significantly mixed with soil air underground. Helium isotopic ratio of Fumarole 4 (Qiqle 4) showed a slight magmatic gas contribution to the fumarolic gas, indicating presence of magmatic heat source beneath the zone of fumaroles.

1. INTRODUCTION

The Republic of Djibouti is located in the Horn of Africa where the geology is also influenced by the Red Sea ridges and Gulf of Aden ridges. It is bordered by Eritrea to the north, Ethiopia to the west and south, and Somalia to the southeast. As part of the geothermal research program, the Djiboutian Office for Geothermal Energy Development (ODDEG) had carried out a surface study on the Arta site. The Arta area is among the 13 potential sites that the Djiboutian Geothermal Energy Development Office wants to develop in the future.

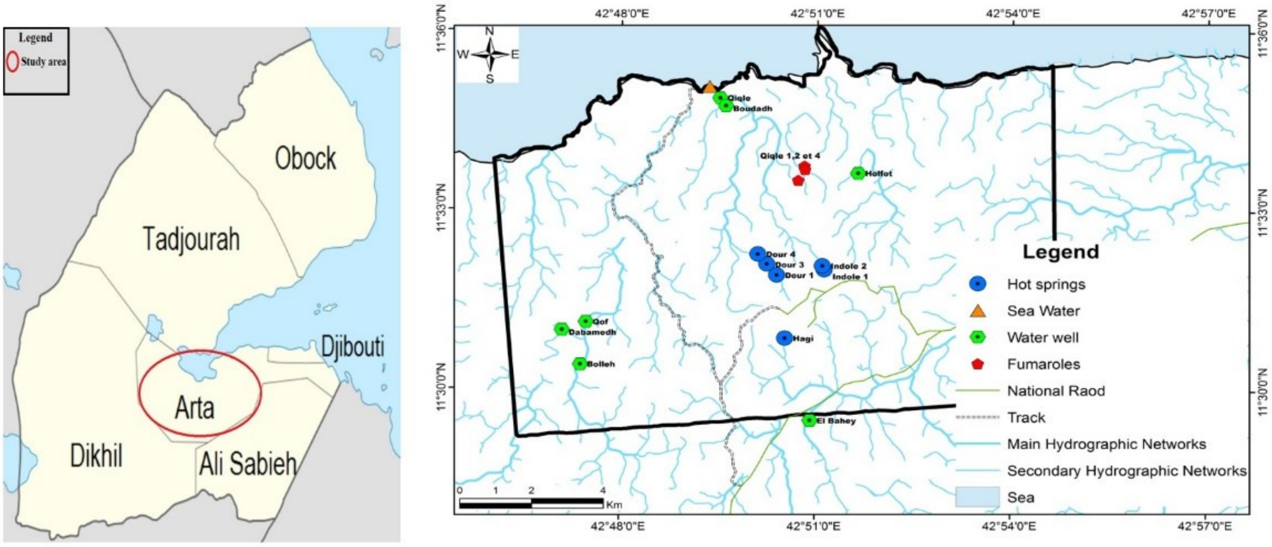


Figure 1: On the left, location map of the Arta study area in Djibouti. To the right, location map of springs, water wells and fumaroles sampled in the Arta area.

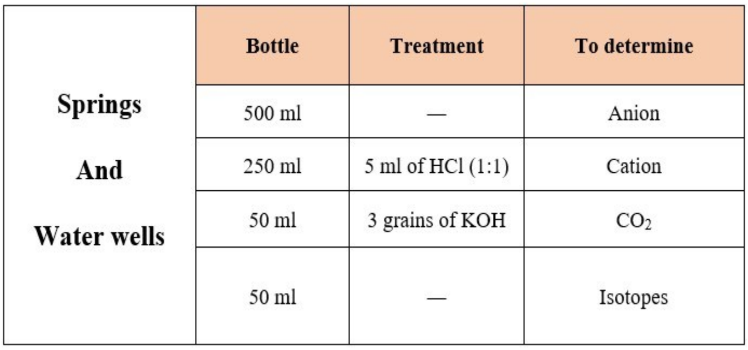
The site of Arta corresponds to a glacis of regular slope constituting the eastern slope of a basalt massif which culminates at about 750 m. The substratum consists of Gulf Basalts whose surface alteration produces rock balls embedded in a clay matrix that is particularly sensitive to erosion due to the weakness of the plant cover (IGN, 1992). It should be noted that the Arta site is located in the immediate vicinity of a zone of high activity: The Gulf of Tadjourah. The Arta region was particularly affected by the seismic crisis of March 1992, which crossed the Gulf of Tadjourah, with a focus of the earthquake located at sea 2 km from the beach of Arta. These earthquakes are a simple consequence of the separation of the Arab and African tectonic plates (B. Didier 2001). This is therefore indicative of the internal activity in the study area. Subsequently, a surface study was conducted to promote the geothermal potential of the Arta region. This study included a geochemical study to identify, sample and analyze water sources, fumaroles and water wells in order to determine their origin, their degree of equilibrium with the rock and the estimation of the internal temperature by geothermometers calculations.

2. METHODOLOGY

2.1 Sampling and measurement on site

Some in-situ measurements were conducted for temperature, pH, conductivity and verification or updating of the coordinates of the sampling locations. For sampling water, pretreatment such as acidification was conducted for proper procedure of chemical analysis (Table 1).

Table 1: Condition of water sampling and pretreatment.



	Bottle	Treatment	To determine
Springs And Water wells	500 ml	—	Anion
	250 ml	5 ml of HCl (1:1)	Cation
	50 ml	3 grains of KOH	CO_2
	50 ml	—	Isotopes

The Normalized Inorganic Charge Balance (NICB), which is the comparison between the sum of the cations (Σ cations) and the sum of the anions (Σ anions) of the water samples, is the simplest way to assess the quality of the analytical data. NICB is given by the following formula (unit is equivalent concentration) and an ideal acceptable value is 3% (+2%). However, in geothermal sites, NICB occasionally exceeds the ideal value. In such case, analytical data is confirmed through repeated analysis.

$$NCIB = \frac{\sum anions - \sum cations}{\sum cations + \sum anions} * 100$$

Table 2: Results of analysis for water samples.

Survey point	Type of water	coordinates		Altimeter	Temperature	pH	EC	SiO2	Cl	SO4	HCO3	Li	Na	K	Ca	Mg	Fe	Al	B	As	δ18O	δD
		Easting	Northing	masl (GPS)	°C	(in site)	mS/cm	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	‰SMOW	‰SMOW
Sea water (ODDEG campsite)	Sea water	265212	1278942	0	30,1	–	49,6	5,6	19900	2740	137	0,19	11600	437	442	1380	<0.01	<0.01	5,4	0,17	0,9	5
Indole 1	Slightly warm spring	265696	1275780	422	39,0	7,7	6,24	80	1690	623	4	0,02	688	11	259	268	<0.01	<0.01	1,6	<0.01	-1,2	-3
Indole 2	Cold Spring	265639	1275910	387	35,1	7,4	7,12	84	1960	692	4	0,03	924	9,5	269	248	<0.01	<0.01	1,9	<0.01	-1,1	-3
Dour 1	Cold Spring	264406	1275678	432	31,1	7,4	12,7	126	3870	1320	5	0,12	1460	3,9	443	747	<0.01	<0.01	3,4	0,12	-0,4	1
Dour 3	Cold Spring	264137	1276017	396	29,2	8,0	14,7	107	4710	1460	4	0,14	1080	3,9	776	1100	<0.01	<0.01	3,0	0,31	0,9	6
Dour 4	Cold Spring	263891	1276326	357	33,5	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Hagi	Cold Spring	264637	1273732	578	31,5	7,6	14,9	34	4200	2150	5	0,05	2240	17	521	526	<0.01	<0.01	2,0	0,10	-0,8	0
Qiqle	Water well	262840	1281140	1	31,2	8,5	5,44	26	1170	425	681	0,02	1170	36	15	21	<0.01	<0.01	2,4	<0.01	-1,2	-7
Qof	Water well	259098	1274251	332	33,3	7,9	0,928	50	75,6	95,2	269	<0.01	160	1,4	20	15	<0.01	<0.01	0,9	<0.01	0,0	-5
Dabamedh	Water well	258424	1274004	304	29,3	7,9	2,43	82	466	174	437	<0.01	286	5,6	60	111	<0.01	<0.01	1,2	<0.01	-1,0	-1
Bolleh	Water well	258930	1272944	361	38,7	8,0	1,45	65	182	152	315	<0.01	253	1,8	36	21	<0.01	<0.01	0,9	<0.01	-0,8	-3
Boudadh	Water well	263004	1280934	13	30,9	8,7	5,40	49	988	430	1060	0,02	1240	31	6,4	12	<0.01	<0.01	2,9	0,09	-1,2	-7
Holfot	Water well	266682	1278827	231	29,0	7,3	5,60	106	1510	325	155	0,04	692	14	202	193	<0.01	<0.01	2,1	0,19	0,1	1
El-Bahay	Water well	265293	1271280	361	31,6	7,6	1,74	109	299	101	251	<0.01	230	2,8	62	50	<0.01	<0.01	0,7	0,07	-1,3	-4

3. RESULTS AND DISCUSSION

The pH values of those water ranging from 7.3 to 8.7 and the temperature of the waters varied 29.0°C to 38.7°C. To determine the nature and the of the water samples we used the following diagrams.

3.1 Classification of the water

3.1.1 Piper diagram

The Piper diagram (Piper, 1944) uses the major ions to present basic chemistry of groundwater. It contains two ternary diagrams showing relative contents of major anions and cations, respectively (cations in the left triangle, anions in the right triangle) as shown in Figure 2.

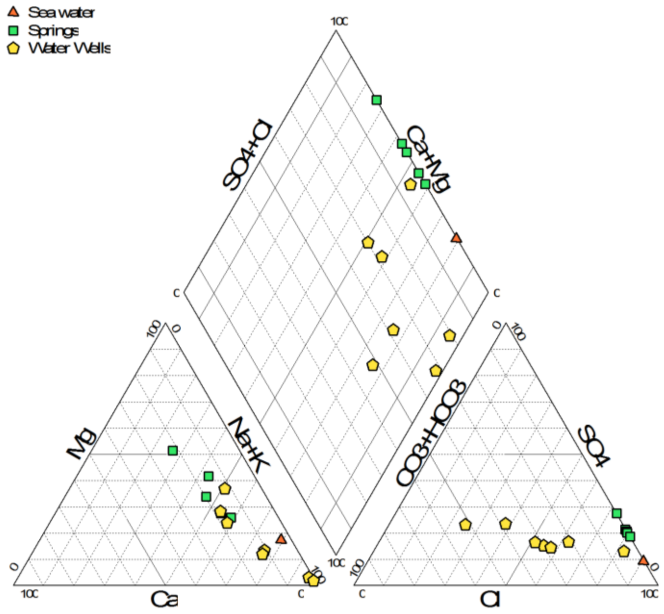


Figure 2: Piper diagram.

The diagram shows that the dominant anion in the spring waters (Indole, Dour, and Hagi, triangle in the figure) is chloride with some sulfate and the cation contents are various. As a result, these waters are a chloride–sulfate type with variation in major cations. On the other hand, the waters wells are chloride type and bicarbonate type. Some of them (Boudadh, Qiqle, Bolleh, and Qof) are rich in sodium and potassium.

3.1.2 Cl-SO4-HCO3 ternary diagram

Cl-SO_4-HCO_3 ternary diagram proposed by Giggenbach (1991) is used to distinguish various types of geothermal waters as shown in Figure 3. The chemistry interpretation of the geothermal water is made on an initial classification with Cl, SO_4 and HCO_3.

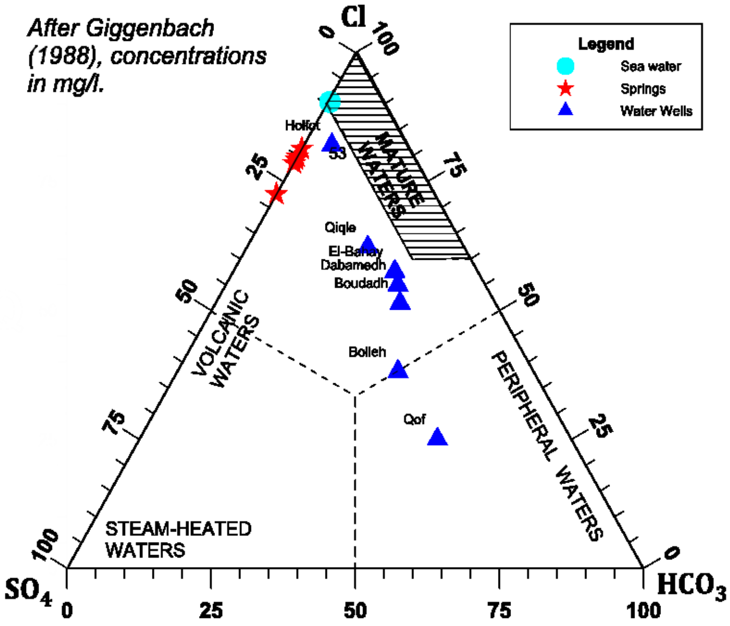


Figure 3: Cl-SO4-HCO3 ternary diagram.

In this diagram, water sample are not classified as mature geothermal waters. The spring waters are plotted along the Cl-SO4 axis of the diagram and this deduces that these waters are of chloride sulfate type. Water wells mix between chloride-sulfate type and bicarbonate type waters.

3.1.3 Na-K-Mg ternary diagram

The Na-K-Mg ternary diagram (Figure 4) proposed by Giggenbach (1988) classifies geothermal waters into three categories: fully equilibrated, partially equilibrated and immature. It is also used to select the most suitable waters for geothermometers and estimate the temperature of the reservoir.

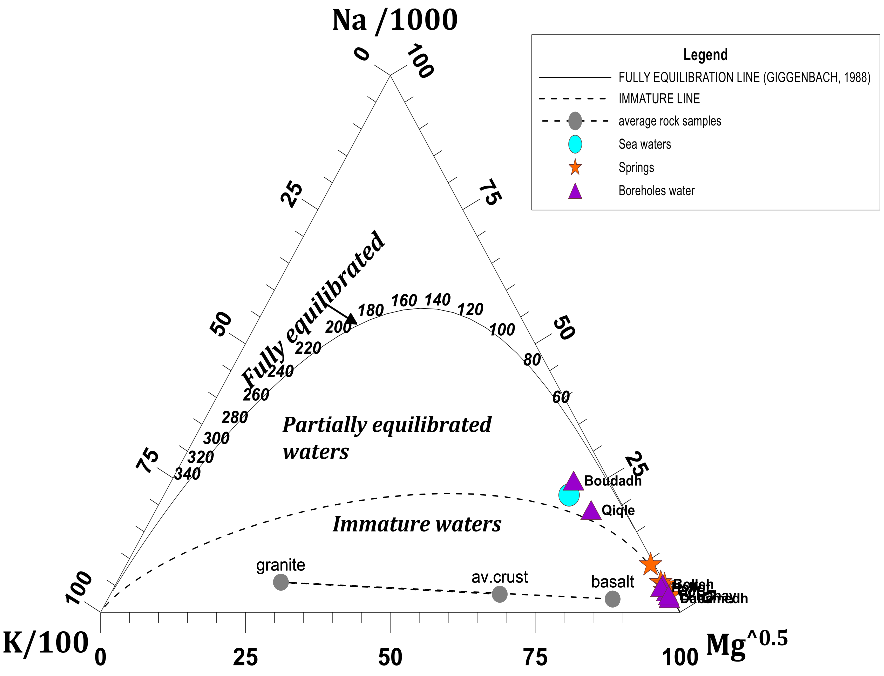


Figure 4: Na-K-Mg ternary diagram.

In the diagram, seawater and water wells Boudadh and Qiqle are the partially equilibrated with rock reservoir. On the other hand, the other samples are classified as immature waters and have high magnesium content, we suggest a large mixing proportion of cold groundwater and hence incompatibility of cation geothermometers for them.

3.2 Origin of the water

3.2.1 B/Cl ratio

The chloride and boron ratio (Cl/B) are used to obtain information on the origin of the waters (White, 1957a, b; White et al., 1963; Truesdell, 1976) and to evaluate the mixing among seawater, magmatic steam, ground water, and evaporated water.

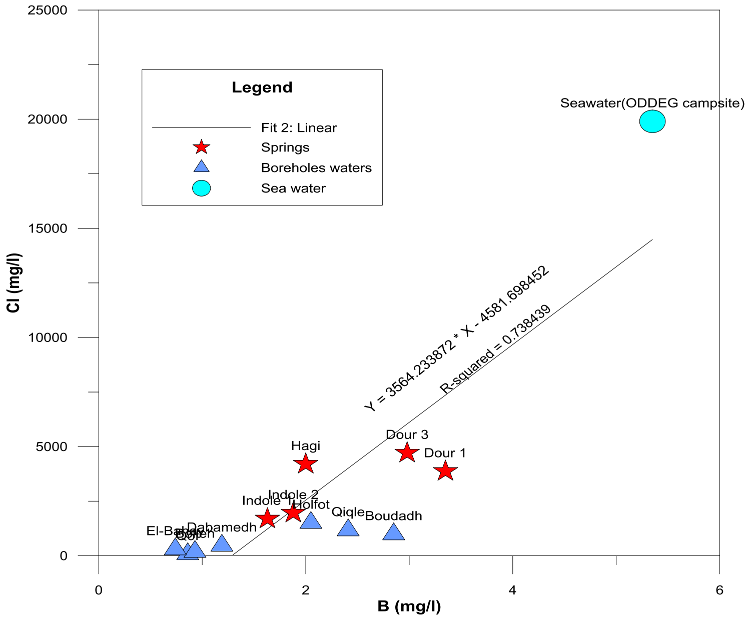


Figure 5: Cl/B Ratio.

In the figure 5, some of water wells (El-Bahay, Dabamedh, Bolleh and Qof) show low concentrations of Cl and B, which probably means that the waters are mainly composed of fresh groundwater. The rest of water well samples and the spring waters show slightly higher values, so that these waters possibly gain Cl and B through the processes such as water-rock interaction, dissolution of evaporite deposit, evaporation in the aquifer, mixing with sea water, or combination of them.

3.2.2 Isotopes

Stable δ18O and δD isotopes are generally used to determine the origin of thermal waters (magmatic or meteoric) and the geothermal reservoir recharge area. Generally speaking, δD and δ18O value of meteoric waters at any locality is dependent upon latitude, altitude and distance from the ocean. In this study area, as shown in Figure 6, the oxygen and hydrogen isotopes can be compared to the global meteoric line (GMWL) and local meteoric line (LMWL). The equations of GMWL and LMWL are defined by Craig (1961) and by Fontes and al. (1980), respectively as follows:

$$\delta D = 8 * \delta^{18}O + 10\ (GMWL)$$

$$\delta D = 8 * \delta^{18}O + 0\ (LMWL)$$

Water from the springs and water wells are plotted along and between GMWL and LMWL, probably indicating that the origin of the waters is local meteoric water.

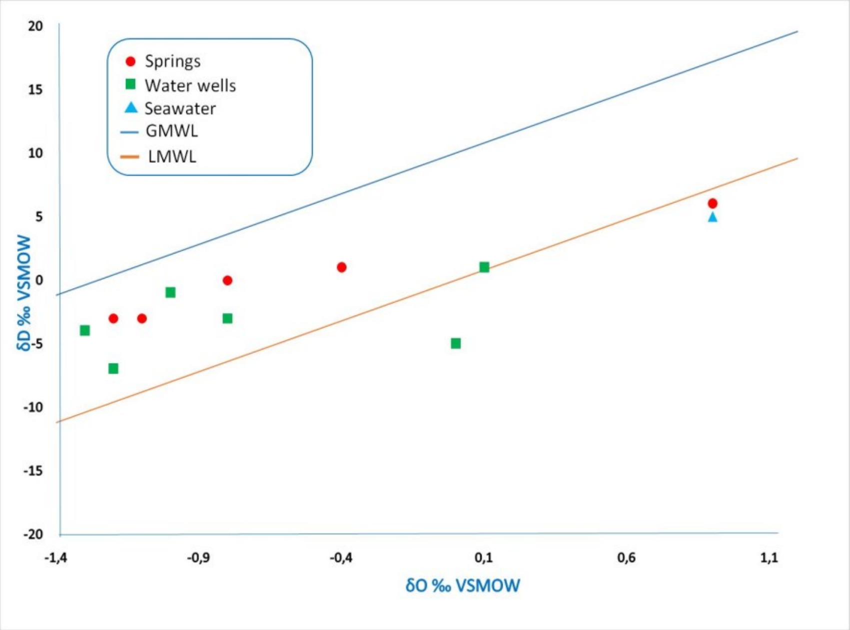


Figure 6: Relationship between hydrogen and oxygen isotopic ratios of geothermal fluid in Arta.

3.3 Gas

In the Arta area, three fumaroles were sampled and analyzed. The results of the analysis are shown in Table 3. In non-condensable gases (NCG), N2 is dominant. Low concentrations of CH4 and Ar are also observed. In particular, CO2 and H2S are not significantly detected in the gas samples.

Table 3: Results of gas analysis.

Survey Site			Arta	Arta	Arta
Sampling Point			Fumarole 1	Fumarole 2	Fumarole 4
Date			16/04/2018	17/04/2018	17/04/2018
Latitude (°N)			11,562358	11,561427	11,558389
Longitude (°E)			42,846980	42,847080	42,845230
T air		(°C)	34,1	35,0	34,2
T fumarole or humid air		(°C)	99,4	97,2	97,4
Boiling point *		(°C)	99,5	99,5	99,4
Intensity of Fumarole			Weak	Very weak	Very weak
H_2O and NCG (total 100%)	H2O	(vol%)	0,00	0,00	0,00
	NCG	(vol%)	100,00	100,00	100,00
NCG composition (total 100%)	H2S	(vol%)	0,0	0,0	0,0
	CO2	(vol%)	0,0	0,0	0,0
	R gas	(vol%)	100,0	100,0	100,0
R gas composition (total ~100%)	H2	(vol%)	0,0006	0,0017	0,0011
	N2	(vol%)	77,8	77,9	77,8
	CH4	(vol%)	n.d.	n.d.	n.d.
	O2	(vol%)	21,4	21,4	21,4
	He	(vol%)	0,0005	0,0005	0,0004
	Ar	(vol%)	0,79	0,78	0,76
$^3He/^4He$		($\times10^{-6}$)	0.0662±0.0057	0.0834±0.0055	1.85±0.09
$^4He/^{20}Ne$		-	58,7	27,8	0,330

3.3.1 N2-He-Ar ternary diagram

The ternary diagram (N2-He-Ar) aims to identify the dominant source of gases (Giggenbach, 1996). This diagram classifies the original gases into four categories; magmatic, air, meteoric (air-saturated water; ASW) and crust gas. In the diagram of N2-H2-Ar (Figure 7), the gas samples are plotted on air component, indicating that the dominant component in the samples is air. The sampled fumaroles were all weak and those temperatures various 97.2°C to 99.4°C. This means geothermal steam had condensed into liquid water during the steam ascending from a deep portion. Accordingly, the emerging steam is practically two-phase fluid of hot moisture (tiny particles of liquid water) and gas.

Considering the rather low temperature and the condensation (cooling) process, the path of ascending steam seems to run through in a thick and cold unsaturated (or vadose) zone, which is between the surface and water table where the ascending steam is cooled. In the unsaturated zone, atmospheric gas (air) is stored in pores. As a result, the separated geothermal gas mixes with considerable atmospheric gas. This mixing process affects greatly when the flow rate of steam is small and/or unsaturated zone is thick. For this reason, it can be said that the sampled gases had already been mixed with air in the soil bed underground before sampling.

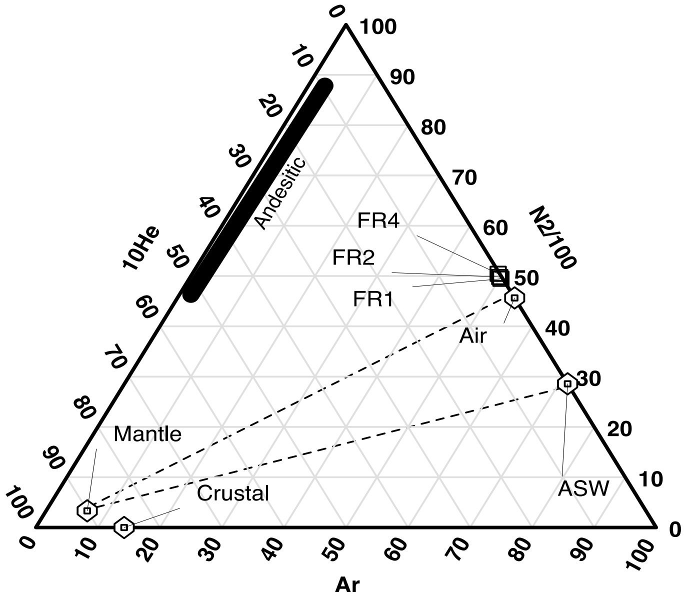


Figure 7: Ternary diagram (N2-He-Ar).

3.3.2 Isotopic $^3He/^4He$ ratio

Noble gas isotopic ratios can be used to estimate contribution of original components of gas to the samples (Lesniak and al., 1997). As shown in Figure 8, the original components are air, mantle (magmatic gas), and crust. Thus, isotopic ratios of noble gases can be an indicator of magmatic gas. In particular, 3He/4He ratio of the sample that is higher than that of air (1.4 ×10-6) is considered such indicator. In Table 3, Fumarole 4 shows that the ratio (1.85×10-6) is slightly higher than that of air. Also, in this Figure 8, Fumarole 4 (FR4) is plotted slightly toward mantle component from air one on the mixing curve. This indicates a slight magmatic gas contribution to the fumarolic gas and hence presence of magmatic heat source beneath the zone of fumaroles.

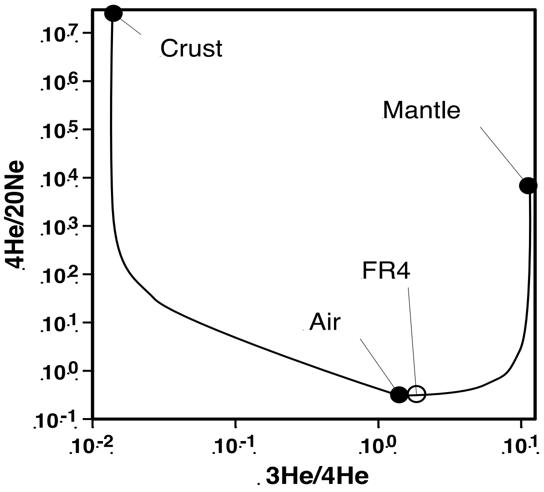


Figure 8: $^3He/^4He$ ratio of noble gases.

3.4 Geothermometers

The geothermometers are used to estimate the reservoir temperature using the chemical and isotope compositions of hot spring water, fumarole and fluid discharge. Geothermometers are probably the most useful application of geochemistry in an exploration phase and made of into three categories (D'Amore, F., and Arnórsson, S., 2000):

1) Solute geothermometers,

2) Gas geothermometers,

3) Isotope geothermometers.

3.4.1 Solute geothermometers (Silica and cation)

Many solute geothermometers have been developed and the most common or "classic" solute geothermometers are the silica geothermometers (e.g., Fournier, 1977), Na/K geothermometers (White, 1965; Ellis, 1969; Fournier and Truesdell, 1973; Fournier, 1979), Na-K-Ca geothermometer (Fournier and Truesdell, 1973), and so on. Regarding silica geothermometers, quartz and chalcedony are chosen for equilibrated minerals in high temperature and low temperature conditions, respectively. In the case where estimated temperature is less than 180°C, chalcedony thermometer is likely more suitable. Accordingly, subsurface temperatures, which is assumed as equilibrium one in the water aquifer, are estimated between 54–125°C for springs and 42-116°C for water wells as shown in Table 4.

Table 4: Results of calculation of geothermometer for water samples.

Sample	Quartz	Quartz	Quartz	Chalcedony	Chalcedony	Na-K	Na-K	Na-K	Na-K	K-Mg	Na-K-Ca
Indole1	125	125	112	97	97	49	98	119	89	34	67
Indole2	128	128	115	100	99	28	77	99	71	32	65
Dour1	151	151	140	125	123	-24	27	48	25	8	36
Dour3	141	141	129	115	113	-14	37	58	35	5	24
Hagi	85	85	70	54	56	14	65	86	60	36	79
Qiqle	74	74	59	42	45	88	133	153	121	88	155
Qof	102	102	88	72	73	21	71	92	65	23	43
Dabamedh	126	127	114	99	98	61	108	129	98	30	67
Bolleh	114	115	101	86	86	12	62	83	57	25	44

Boudadh	101	101	87	71	72	75	121	142	110	91	153
Holfot	140	141	129	114	112	62	110	130	100	42	80
El-Bahay	142	142	130	116	114	36	85	106	78	25	45
Reference	Founier (1977)	Founier & Potter (1982)	Arnorsson and al. (2000)	Founier (1977)	Arnorsson and al. (2000)	Truesdell (1976)	Fournier (1979)	Giggenbach (1988)	Arnósson (2000)	Giggenbach (1988)	Founier and Truesdell (1973)

4. CONCLUSION

Geochemical data of springs, water wells and gas from fumaroles was carried out in order to determine the characteristic and the origin of the reservoir in this area as well as to estimate reservoir temperatures.

According to classification diagrams, it can be concluded that nature of the springs is of the chloride-sulphate type while the well waters varies in chloride and in bicarbonate type. The same samples of water (Boudadh, Qiqle, Bolleh and Qof) are rich in cation sodium and potassium of cation. Based on the Na-K-Mg ternary diagram, two water wells (Boudadh and Qiqle) are possibly partially equilibrated with rock or affected by the seawater mixture. The other samples are considered to be immature water.

With regard to gases, the ternary diagram N2-He-Ar showed us that the fumaroles of the Arta region showed a low flow rate because the gases were mixed significantly with the soil air in the ground underground. There is a slight contribution of the magmatic gas to the fumarolic gas, indicating the presence of a source of magmatic heat under the area of the fumaroles in accordance with the isotopic ratio of helium (^{3}He / ^{4}He) from the Fumarole 4.

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