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Geochemical Study of Arta, Djibouti

Sadik Bachir, Liban Imael, Daisuke Fukuda, Rokiya Houssein, Daher Ali, Ayan Ahmed, Kayad Moussa, Nasradine Ahmed

Djiboutian Office for Development of Geothermal Energy (ODDEG)

Under Presidency

P.O. Box 2025, Djibouti

sadik.bachir@oddeg.dj, libanismaeldarar@gmail.com, fukuda@geothermal.co.jp, rokiya.houssein@oddeg.dj, daher.ali@oddeg.dj, ayan.ahmed@oddeg.dj, kayad.moussa@oddeg.dj, nasradine.ahmed@oddeg.dj

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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 five hot 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 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.

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.

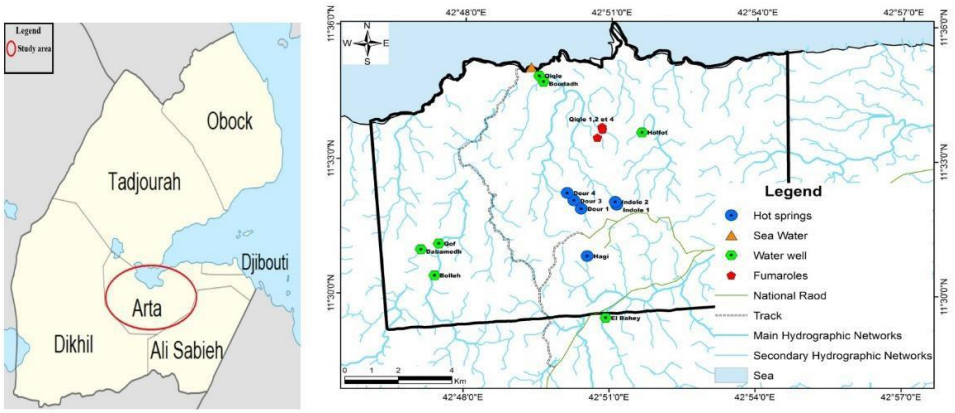


Figure 1: On the left, location map of the Arta study area in Djibouti. To the right, location map of springs, water wells and fumaroles sampled in the Arta area.

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 determined
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

2.1.1 Quality of chemical data

Data quality is a fundamental element for consecutive interpretation. It must be shown that small analytical errors can occur.

The Normalized Inorganic Charge Balance (NICB), which is the comparison between the sum of the cations (Σcations) and the sum of the anions (Σanions) 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
Qigle	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

Waters of springs and water wells in the Arta area possessed pH values ranging from 7.3 to 8.7. The temperature of the waters varied from 29.0°C to 38.7°C. To study the nature of the water samples, the following diagrams were used to visualize the analytical data.

3.1 Classification of the water

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.

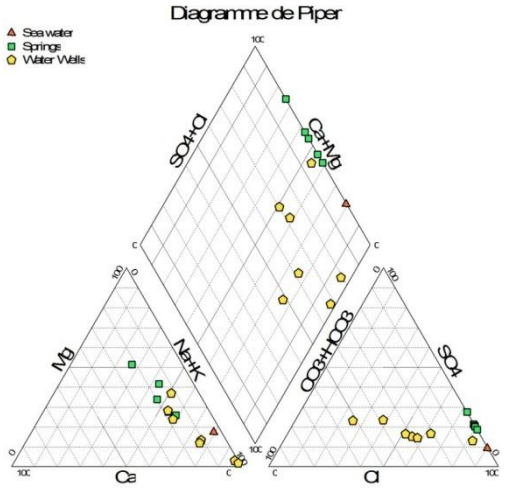


Figure 2. Piper Diagram

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 from water wells vary in chloride and bicarbonate contents on anion diagram. Some of them (Boudadh, Qiqle, Bolleh, and Qof) are rich in sodium and potassium on cation diagram.

Cl-SO_4-HCO_3 ternary diagram

Cl-SO_4-HCO_3ternary diagram proposed by Giggenbach (1991) is used to distinguish various types of geothermal waters as shown in Figure 3. The interpretation of the chemistry of the geothermal water is made on an initial classification with Cl, SO_4 and HCO_3. Note that this diagram fundamentally explains the chemical characteristics of geothermal water in subduction-type geothermal activities.

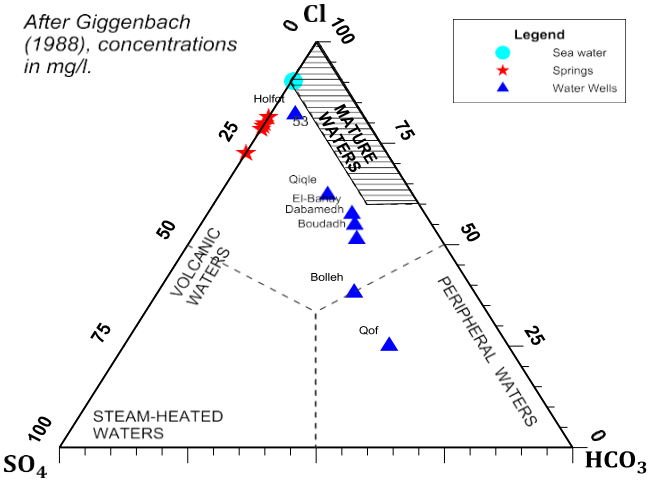


Figure 3. Cl-SO_4-HCO_3 ternary diagram

In this diagram, all sampled waters are not classified as mature geothermal waters. The spring waters are plotted along the Cl-SO_4axis of the diagram, showing that the waters are chloride-sulfate type. Water wells show mixing between chloride-sulfate type and bicarbonate type waters.

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 geothermometry and estimate the temperature of the reservoir.

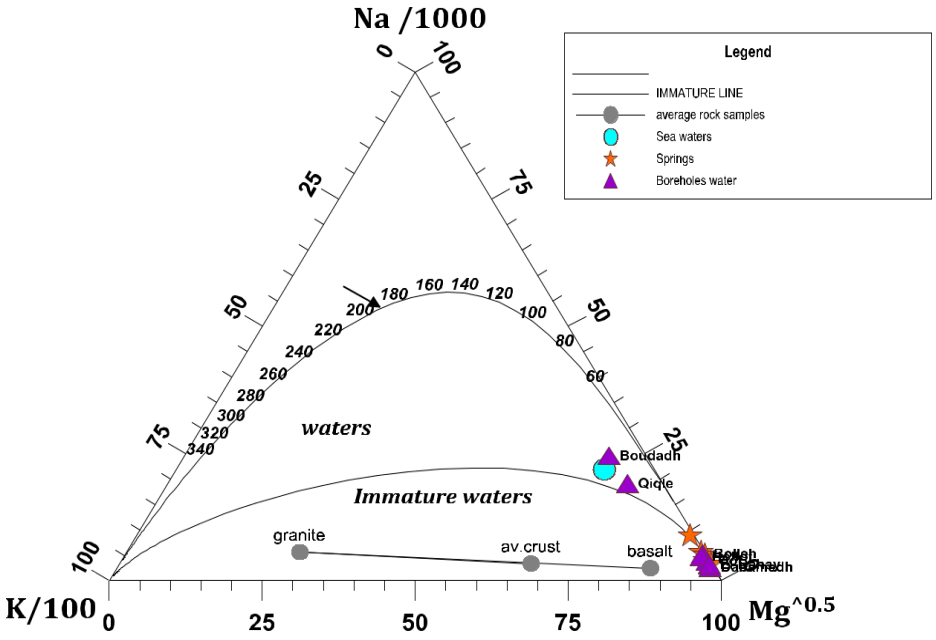


Figure 4. Na-K-Mg Ternary Diagram

In the diagram, seawater and water wells Boudadh and Qiqle are plotted in the partially equilibrated part, which possibly indicates that the water-rock reaction of the waters proceeds to some extent compared to the other waters, or the waters gain the property of partially equilibrated seawater through the mixing process. On the other hand, the other samples are classified as immature waters with high magnesium content, suggesting a large mixing proportion of cold groundwater and hence incompatibility of cation geothermometers for them.

3.1.1 Origin of the Water

B/Cl ratio

The chloride and boron ratio (Cl/B) is 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.

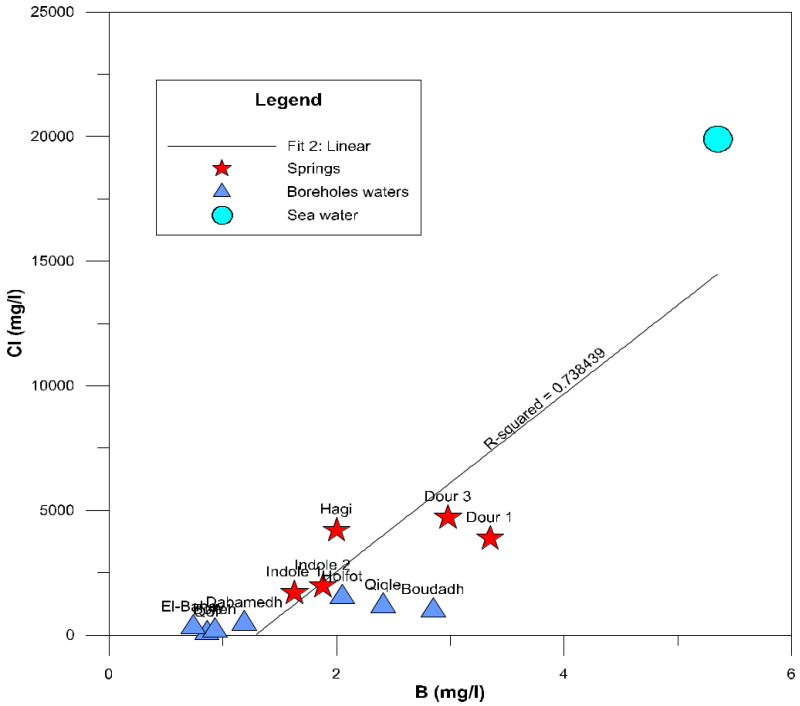


Figure 5. Cl/B Ratio

In the figure, 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 Cl and B concentrations of 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 evaporate deposit, evaporation in the aquifer, mixing with sea water, or combination of them.

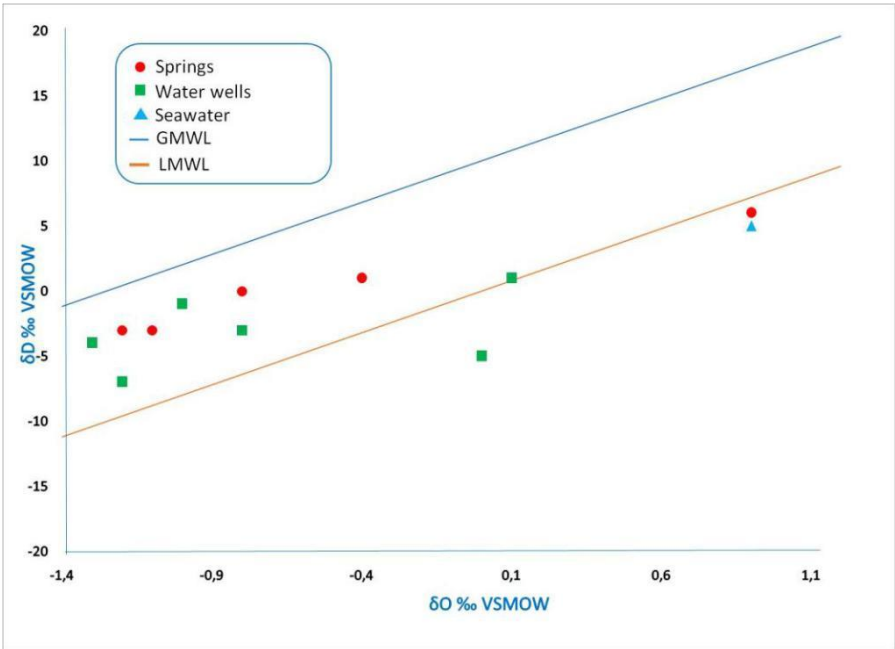
Similarity of concentrations of B and Cl among the samples was found in two locations. One is a zone including Dabamedh, Qof, and Bolleh, and the other Qiqle and Boudadh. In these zones, local characteristics of geology may control the concentrations of the waters.

Isotopes

Stable $\delta^{18}O$ and δD isotopes are genrerally used to determine the origin of thermal waters (magmatic or meteoric) and the geothermal reservoir recharge area.Generally speaking, δD and $\delta^{18}O$ 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 et al. (1980), respectively as follows:

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



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

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

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.

3.2 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), N_2 is dominant. Low concentrations of CH_4 and Ar are also observed. In particular, CO_2 and H_2S 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	Veryweak	Veryweak
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
$^3He/^4He$		($\times 10^{-6}$)	0.0662±0.0057	0.0834±0.0055	1.85±0.09
$^4He/^{20}Ne$		-	58,7	27,8	0,330

N_2-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. As shown 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 or faint, showing temperatures (97.2°C to 99.4°C) lower than those of a boiling temperature of pure water. 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.

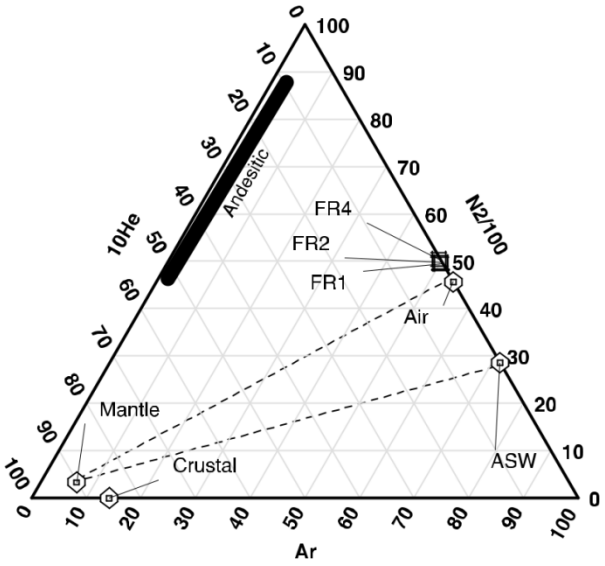


Figure7. Ternary Diagram (N2-He-Ar)

Isotopic $^3He/^4He$ ratio

Noble gas isotopic ratios can be used to estimate contribution of original components of gas to the samples (Lesniak et 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 4shows that the ratio (1.85×10-6) is slightly higher than that of air. Also, in this Figure, 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.

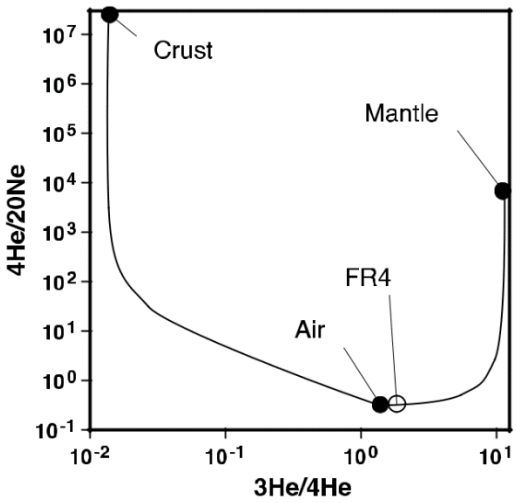


Fig 8. $^3He/^4He$ ratio of noble gases

3.2.1 Geothermometer

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

1) Solute geothermometers,

2) Gas geothermometers,

3) Isotope geothermometers.

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 et al. (2000)	Founier (1977)	Arnorsson et al. (2000)	Truesdell (1976)	Fournier (1979)	Giggenbach (1988)	Arnósson (2000)	Giggenbach (1988)	Founier & Truesdell (1973)

CONCLUSION

Analyses of geochemical data of springs, water wells and gas from fumaroles was carried out in order to estimate the subsurface reservoir temperatures and to investigate the origin of the waters.

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.

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