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Geochemical study of Hanle geothermal prospect, Djibouti

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ABSTRACT

The Republic of Djibouti is located in East Africa, in the Great Rift Valley and Afar Triple Junction. From a geological point of view, the Hanle lava plateau is composed of basaltic lava layers called the Afar Stratoid Series. Faults or fractured systems were formed in the NW-SE direction in the plateau. Hydrothermal activities are found in fumaroles with temperatures higher than 98°C and a hot spring. Using the chemical compositions of the fumaroles and hot springs, reservoir temperature was estimated to be 180°C–260°C with gas geothermometers and 125°C with a solute geothermometer. The major solute components of the hot spring suggest that the spring water is created by the mixing of groundwater and heated fossil seawater or the dissolution of evaporating by heated groundwater. In that area, geothermal steam discharges most vigorously at Garabbayis and Goros. These zones can be a prospect for subsequent exploration including test drilling.

1. INTRODUCTION

The Republic of Djibouti spans a surface area of 23,000 km2 and is located in the Horn of Africa in the East African Rift system between Somalia and Ethiopia. The study area, Hanle plain, which is located in the vicinity, is highly fertile and is relatively inhibited. However, the absence of local energy resources in this area causes a delay in the development of the area. Due to its distance from the electric line, the Dikhil region, supplied its electricity from a modest diesel plant (Figure 1).

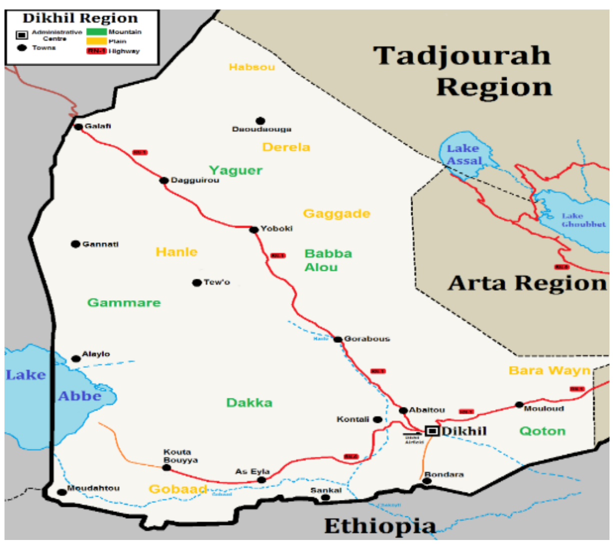


Figure 1. Map of the south-western part of Djibouti Republic.

In the survey, samples were taken in January and September 2016 from water wells (groundwater), a hot spring, and fumaroles (gas or steam condensate). The samples were analyzed in Japan. The main objectives of the present study are to interpret the gas and water geochemistry by classifying the thermal waters using a ternary diagram, to estimate the reservoir temperature with geothermometers (quartz, cation and gas) and to determine the origin.

2. METHODOLOGY

2.1 Survey site

At Garabbayis, Garabbayis North, Adha'amo, Goros, Dimbil, Dirdir, and Lafofili, fumarolic gas were sampled. Specifically, at Garabbayis steam condensate was also collected. Only at Kori was discovered a hot spring. Four water wells were collected and Figure 2 and Table

1 depict the sampling sites and the field records. In Garabbayis, steam condensate rather than gas was collected for isotopic interpretation with groundwater. In Garabbayis, steam condensate rather than gas was collected for isotopic interpretation with groundwater. The Kori hot spring was sampled twice in January and September and the temperature varied between January and September. The center region of the Hanle lava plateau is covered in geothermal manifestations, including fumaroles and a hot spring, as depicted in Figure 2.

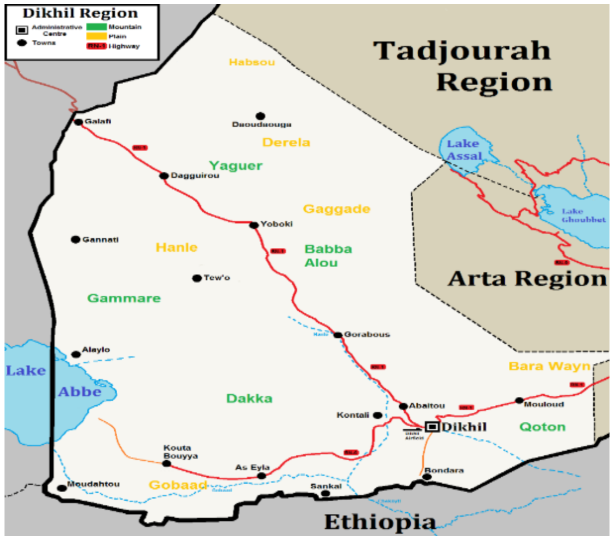


Figure 2. Sampling location map of the geochemical survey in 2016.

Table 1. Records of sampling sites.

Code number	**Manifestation**	**Location**	**Date**	**Coordinate**	**Sample temperature (°C)**	**pH**	**EC (µS/cm)**
HNL2016_001	Fumerole	Dirdir	22/01/2016	N°11,434015 E°42,27948 114 m	113,8	-	-
HNL2016_004	Fumerole	Dimbil	24/01/2016	11,458735 42,235676 483	97,1	-	-
HNL2016_007	Water Well	Dirdir	27/01/2016	11,449567 42,268527 88	28,8	7,5	4170
HNL2016_002	Fumerole	Adha'amo	23/01/2016	11,44689 42,185024 402	98,5	-	-
	Fumerole	Garos		11,458625	102,1	-	-

HNL2016_003			23/01/2016	42,211182 426			
HNL2016_005	Hot, wet ground (soil)	Lafofili	25/01/2016	11,338409 42,219727 278	108,8	-	-
HNL2016_006	Fumerole	Garabbayis north	26/01/2016	11,416357 42,174038 335	100,9	-	-
HNL2016_008	Hot spring	Kori	28/01/2016	11,366576 42,287346 208	48	7,8	3780
HNL2016_009	Fumerole (steam condensate)	Garabbayis	29/01/2016	11,407929 42,179844 284	99,7	-	-
HNL2016_010	Water Well	Garabbayis (dug well)	25/09/2016	11,39845 42,151581 213	32,6	8,3	1037
HNL2016_011	Water Well	Cheksabir	26/09/2016	11,269502 42,229271 300	38,5	7,9	1279
HNL2016_012	Water Well	Garos (dug well)	27/09/2016	11,460372 42,210178 400	34,8	8,1	711
HNL2016_013	Hot spring	Kori	29/09/2016	11,366576 42,287346 208	53,8	8	1617

Table 2: Sample treatment and analytical methods for geothermal water and gas.

Phase	Treatment	Specification	To determine	Analytical method
Liquid	None, amber glass bottle with airtight stopper	Ru	pH, conductivity, CO_2, H_2S *(In situ)*	Potentiometry, Titrimetry
	Dilution; 50 mL of sample + 50 mL of distilled, deionized water	Rd (1 :1)	SiO_2 if > 100 ppm	Spectroscopy with ammonium molybdate
	Filtration	Fu	F, Cl, Br, SO_4, B	Ion chromatography, Spectroscopy
	Filtration; 0.8 mL of HNO_3 added to 200 mL sample	Fa	Na, K, Mg, Ca, Fe	Atomic absorption spectroscopy
	Filtration; 2 mL of 0.2 M $ZnAc_2$ + 98 mL of sample	Fp	SO_4	Ion chromatography
	Filtration	Fu	^{2}H, ^{18}O	Mass spectrometry
Vapor	None; amber glass bottle	Ru	^{2}H, ^{18}O	Mass spectrometry
	None	Ru	Anions	Ion chromatography
	0.4 mL conc. HNO_3 (Suprapur) added to 100 mL sample	Ra	Cations	Atomic absorption spectroscopy
	Added to 50 mL 40% NaOH in evacuated double port bottle	Gas sample	H_2, CH_4, N_2, O_2, Ar CO_2, H_2S in NaOH	Gas chromatography, Titrimetry

2.2.2 Sampling of fumarole

It is more difficult to choose a fumarole for sampling than a hot spring. In locations exhibiting the most severe acid surface change, it is typically advisable to sample small outlets that discharge steam at a significant flow rate. A NaOH solution should be made in the lab and placed in a double port bottle before the sampling. The bottle should then be evacuated. While the other gases remain in the bottle's headspace, the CO2 and H2S present in the steam quantitatively dissolves in the alkaline solution. Additionally, samples of condensed steam are collected. In an airtight amber glass bottle, a portion is collected for analysis of stable isotopes of oxygen and hydrogen along with an untreated fraction for Cl, B, and Na analyses (Table 2).

2.2.3 Sampling of springs

The water should be flowing from the sampling location while taking samples from hot springs. A sample pump is required if not. Both the outflow and water temperature are noted. In order to evaluate pH, CO2, H2S, and conductivity, an untreated sample is gathered and placed in an airtight container. For SiO2 measurement, the sample is diluted with distilled and deionized water to have an optimal concentration of 30 to 100 ppm if the subsurface temperature is anticipated to be high. For anions, a filtered sample is taken, while for cations, a filtered and acidified sample is collected.

HNO3 acid was employed as the acid, and the filter and membrane had pores with a size of 0.45 m. The sample is filtered and sulfide is precipitated using zinc acetate, Zn (CH3COO)2, in order to evaluate SO4. The material is filtered and collected in an airtight 60 mL glass bottle for the analysis of stable isotopes. Table 2 provides a detailed description of the various sub-samples gathered.

2.2.4 Chemical analysis

Conductivity and water temperature are measured in-situ, and the pH and CO2, and H2S concentrations in samples are examined the same day in a field laboratory. The geochemistry laboratory analyzes the primary chemical components in water samples using the analytical techniques listed in Table 2.

3. RESULTS AND DISCUSSION

3.1 Gas results

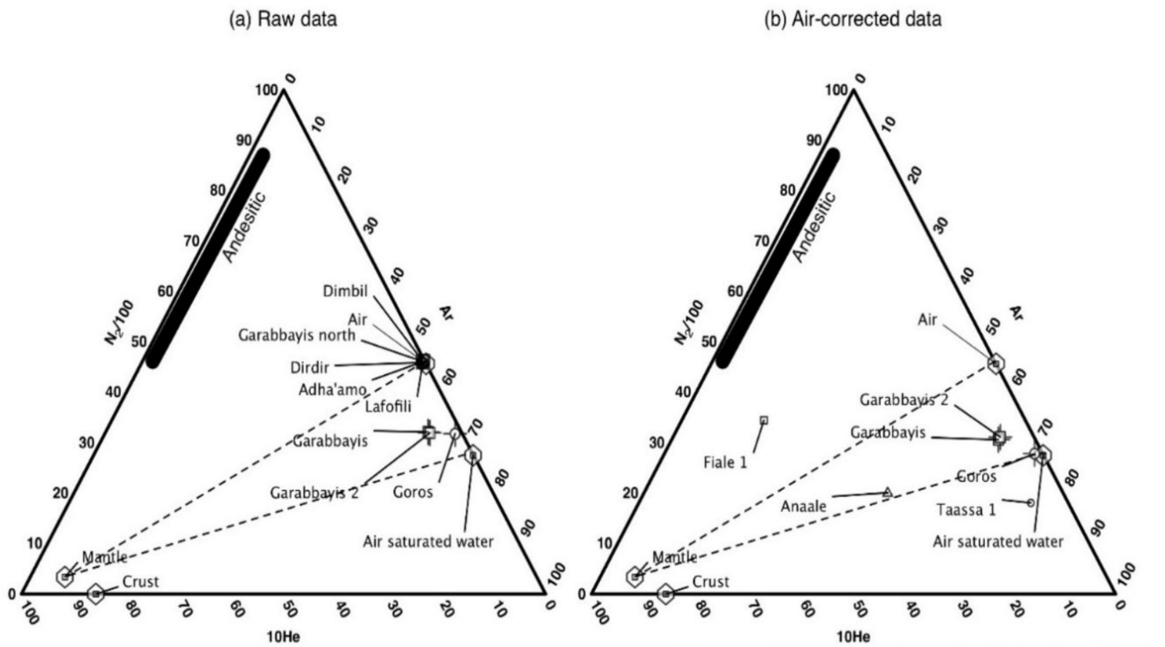
The chemical compositions of the gases were rectified by removing the atmospheric component from the assessed compositions (Table 3) because the fumarolic gas samples contain the atmospheric component (i.e., air) in significant amounts. The sample must have a geothermal component at a specific high concentration in order for the correction to work. The following gases, CO2, H2S, N2, H2, CH4, and NH3 are present in geothermal discharges. So, it is important to know the behavior of these geothermal gases.

Table 3. Chemical composition of the fumarolic gas corrected for the atmospheric component.

Survey Site			Hanle	Hanle *1	Hanle *2
Sampling Point			Goros	Garabbayis	Garabbayis
Location No.			HNL2016_003	No. 2	No. 1
Date			23/01/2016	07/04/2015	30/05/2014
Latitude (°N)			11,458625	11,407561	11,406481
Longitude (°E)			42,211182	42,180200	42,180689
T air		(°C)	32,4	39,3	32,3
T fumarole		(°C)	102,1	98,8	99,8
Boiling Point		(°C)	98,7	99,0	99,5
Intensity of Fumarole			Moderate	Relatively strong	Relatively strong
H2O and NCG (total 100%)	H2O	(vol%)	99,98	99,98	99,98
	NCG	(vol%)	0,02	0,02	0,02
NCG composition (total 100%)	H2S	(vol%)	36,9	13,0	0,0
	CO2	(vol%)	0,0	16,1	49,7
	R gas	(vol%)	63,1	70,9	50,3
R gas composition (total ~100%)	H2	(vol%)	2,7	0,070	0,066
	N2	(vol%)	94,4	96,9	96,6
	CH4	(vol%)	0,47	1,1	1,2
	He	(vol%)	0,0053	0,020	0,022
	Ar	(vol%)	2,4	2,0	2,1
t_{HA} *3		(°C)	179	74	72
t_{CA} *3		(°C)	–	121	159
t_{MC} *3		(°C)	–	234	266

3.1.1 N2-He-Ar ternary diagram

The relative concentrations of He, Ar, and N2 in fumarolic gases are shown in Figure 3. With the exception of Garabbayis and Goros, Figure 3 (a) was realized from investigated raw data and shows that the composition of fumaroles is almost identical to that of the atmospheric (air) component. Figure 3 (b) uses air-correlated composition, which is created by subtracting the studied composition from the composition of the air, to represent fumaroles from the Garabbayis, Goros, and other species. As can be seen in the image, Garabbayis has the mantle component, however, Goros is missing the component's signature. The presence of mantellic components could indicate the presence of magma as the heat source of this geothermal system.

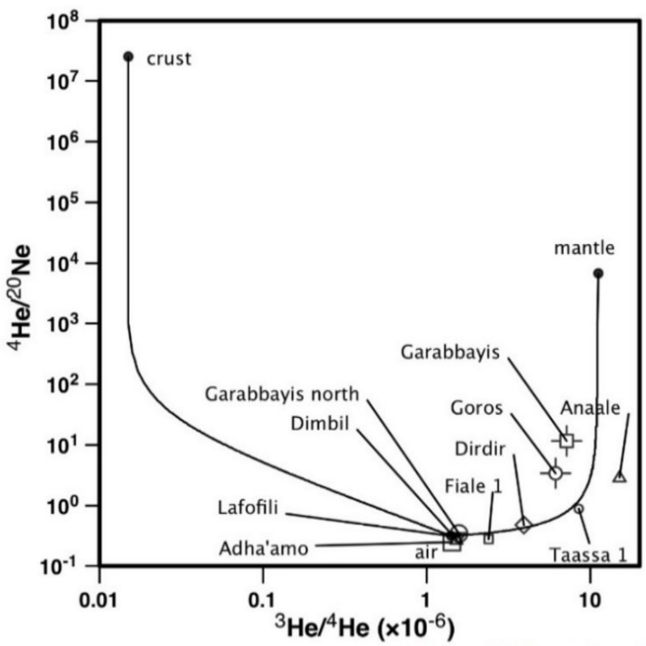


Source: JICA Survey Team, JICA (2014 and 2015)

Figure 3. Relative He, Ar and N2 contents of fumarolic gases.

3.1.2 Isotopic ratio

Analysis of the isotopic ratios of noble gases has been done in order to determine the contribution of the mantle component. The fumaroles are plotted along the mixing curve of the atmospheric (air) and mantle components, as can be seen in a correlation diagram of 3He/4He and 4He/20Ne (figure 4). Garabbayis fumarole is probably supplied with mantle gases from the heat source. The contribution of the mantle component for Garabbayis is higher than the Goros abd Dirir fumaroles. It can be detected in both the relative concentrations of He, Ar, and N2 and the isotopic ratios of noble gases.



Source: JICA Survey Team, JICA (2014 and 2015)

Figure 4. Relationship between $^3He/^4He$ and $^4He/^{20}Ne$ of fumarolic gases.

3.1.3 Gas geothermometers

Gas geothermal thermometers, which use ratios of H2/Ar, CO2/Ar, and CH4/CO2 (Giggenbach, 1991), were applied to the gas composition of Goros and Garabbayis by use of air-corrected chemical data. In Table 3, the calculated results are shown as tHA for H2/Ar thermometer, tCA for CO2/Ar thermometer, and tMC for CH4/CO2 thermometer. The maximum temperatures are 179 °C (tHA) and 266 °C (tMC) for Goros and Garabbayis, respectively. As a result, the reservoir temperature is estimated to be 180°C–260 °C (JICA, 2015).

3.2 Water results

Some chemical parameters were analyzed directly at the site such as pH, conductivity, and temperature of each sample. The results are presented in Table 4.

3.2.1 Cl-SO4-HCO3 diagram

The Cl-SO4-HCO3 diagram classifies geothermal waters using the major anion concentrations. It distinguishes the waters as mature, peripheral, volcanic, or steam-heated. The location of the Kori hot spring in Figure 5 indicates that this water is mixed with groundwater. The data shows that the relative content of Cl in the Kori hot spring in September is low compared to January 2016. It can be interpreted probably by an increase in the mixing ratio of groundwater.

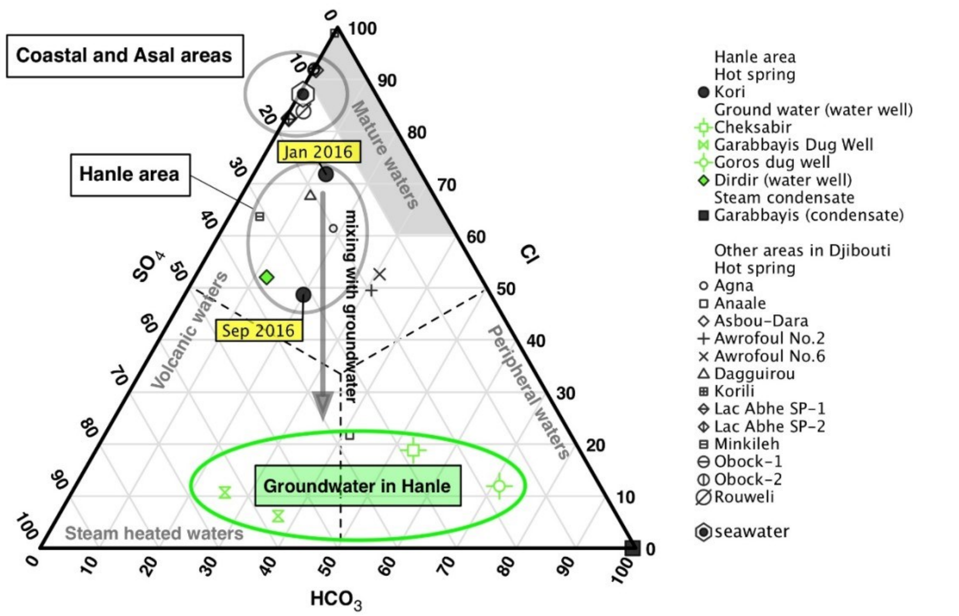


Figure 5. Relative Cl, SO4, and HCO3 contents of water samples.

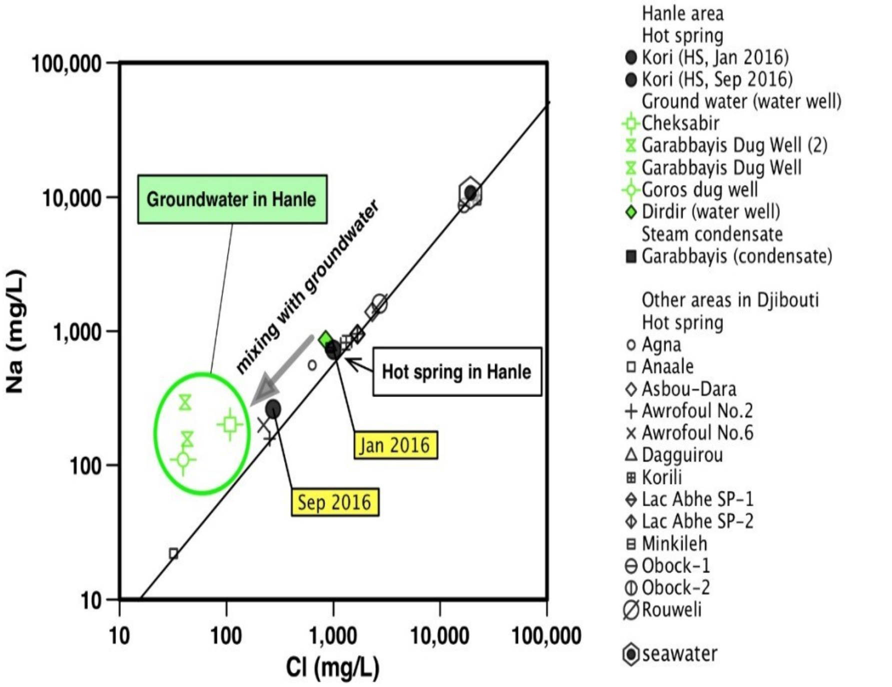
3.2.2 Origin of the water

The relationship between the levels of Na and Cl in hot springs and groundwater is shown in Figure 6. This figure shows that the groundwater has a reduced relative content and concentration of Cl, with the exception of the Dirdir water well. Hot springs plots in the Hanle region roughly exhibit a pattern that mimics the groundwater's chemical components in the picture. This fact suggests that the original hot spring water and diluted groundwater have been combined. The same data demonstrates that Cl concentration and relative content in Kori were lower in September than they were in January. An increase in the groundwater mixing ratio can be used to explain this variation.

Reservoir has been formed in wide area as a results of thermal flow convection recharged by meteoric water. Geothermal fluid should be recharged from the Hanle Plain where groundwater level is higher thanin the plateau. Source of fluid could be derived from Ethiopian side (mountain side).

Table 4. Results analysis for water samples (JICA source).

Sample	Type	Date	Temp	pH	EC	SiO_2	Cl	SO_4	HCO_3	F	Na	K	Ca	Mg	Al	Fe	B	As	δD	$\delta^{18}O$
			°C	-	µs/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
Dirdir	Water well	27/01/2016	28.8	7.5	4170	65	852	589	198	8.7	862	3.6	47	4.8	<0.01	0.02	2.7	0.016	-21	-2.5
Garabbayis (dug well)	Water well	25/09/2016	32.6	8.3	1037	25	43	256	104	1.1	156	6.8	36	3.4	<0.01	<0.01	0.51	<0.001	9	1.1
Cheksabir	Water well	26/09/2016	38.5	7.9	1279	51	108	160	306	1	201	5.7	21	24.4	<0.01	<0.01	0.43	0.001	0	-0.6
Goros (dug well)	Water well	27/09/2016	34.8	8.1	711	36	39	55	232	0.36	110	2.3	24	3.1	0.06	0.14	0.24	0.003	2	0.1
Kori	Hot spring	28/01/2016	48	7.8	3780	131	1000	224	169	2.6	724	20	50	4	<0.01	<0.01	0.61	0.018	-5	-0.4
Kori	Hot spring	29/09/2016	53.8	8	1617	101	273	176	112	2.2	262	14	29	3.6	<0.01	<0.01	0.35	0.004	-1	0
Garabbayis	Steam condensate	29/01/2016	99.7	5.8	36	0.11	0.04	0.73	153	<0.01	<0.01	<0.01	0.04	0.01	<0.01	0.02	0.01	<0.01	-51	-8.5

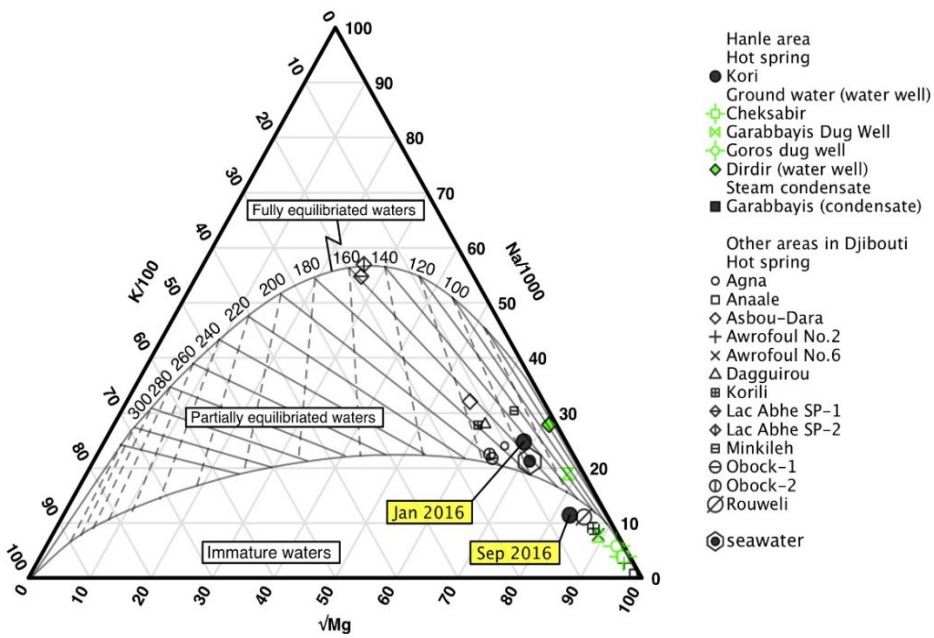


Source: JICA Survey Team, JICA (2014)

Figure 6. Relationship between Na and Cl water samples.

3.2.3 Na-K-Mg diagram

The Na-K-Mg diagram is used to know the water-rock interaction and to estimate the reservoir temperature. This diagram (Figure 7) shows that the Kori hot spring is partially equilibrated with rock in January. It means that the temperature conditions in the subsurface area allow a water-rock interaction. On the other hand, in September, the Kori hot spring is plotted in immature water that is out of partial equilibrium. This is probably due to the fact that groundwater diluted the Kori hot spring water in September more than in January.



Source: JICA Survey Team, JICA (2014)

Figure 7. Relative Na, K and Mg contents of water samples.

3.3 Geothermometers

3.3.1 Silica and Cation Geothermometers

In this paper, seven geothermometers equations were used (table 5): three for Na-K, one for chalcedony, one for quartz, one for K-Mg one Na-K-Ca. This table presents the results of the geochemical thermometer calculations based on the chemical composition of the Kori hot spring. In the Hanle region, weak alteration of rock is observed, for that chalcedony geothermometer was chosen. The result of chalcedony indicates that the hot spring aquifer has a temperature of about 125°C, which is shallower than the geothermal reservoir.

Table 5. Results of calculation of geochemical thermometers for the Kori hot spring.

Sample	Date	Manifestation	Temperature measured (°C)	Geothermometers (°C)						
				Quartz	Chalcedony	Na-K (A)	Na-K (F)	Na-K (G)	K-Mg (G)	Na-K-Ca
Kori	2016/1/28	Hot spring	48.0	142	125	115	127	147	94	134
Kori	2016/9/29	Hot spring	53.8	126	110	153	169	187	86	153

Reference of geothermometers: quartz from Arnórsson (2000), chalcedony from Arnórsson et al. (1983), Na-K(A) from Arnórsson (2000), Na-K (F) from Fournier (1979), Na-K (G) and K-Mg from Giggenbach (1988), Na-K-Ca from Fournier and Truesdell (1973)

Source: JICA Survey Team

4. CONCLUSION

Analyses of geochemical data of thermal waters from hot springs and gas from fumaroles were carried out in order to estimate the subsurface reservoir temperatures and to investigate the origin of the gas. Fumarolic gas of Hanle is mostly composed of atmospheric components and only Garabbayis fumarole is fed with gas from the heat source. The thermal water of Kori is classified as mixed water with groundwater using the Cl-SO4-HCO3 ternary diagram. The Na-K-Mg ternary diagram indicates that the Kori hot spring is partially equilibrated with rock in January.

The reservoir temperatures were estimated using various solute geothermometers which were found to be 125°C. This is in accordance with the Na-K-Mg ternary diagram which gives a similar range of temperature. The gas geothermometer was used to estimate the reservoir temperature of the Hanle geothermal area. It ranged between 180°C and 260°C. Finally, geochemical studies and field observations suggest that the study area is a high-temperature geothermal system, which has to be confirmed by drilling.

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