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Hydrogeochemistry and hydrothermal alteration of the Hanle geothermal field, Djibouti-East Africa

Hanle jeotermal alanının hidrojeokimyası ve hidrotermal alterasyonu, Cibuti-Doğu Afrika

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Abstract

This study focuses on the geochemistry and hydrothermal alteration of the Hanle geothermal field (Djibouti-East Africa). Water from five drinking water wells, a hot spring and a steam condensate in the Hanle graben was analyzed for major and minor hydrogeochemical parameters. Analyzed items for water samples (hot spring water, groundwater, and steam condensate) are pH, electric conductivity (EC), SiO_2, Cl, SO_4, HCO_3, F, Na, K, Ca, Mg, Al, Fe, B, As, δD, $\delta^{18}O$. Using the chemical compositions and saturation indexes of the hot springs, the reservoir temperature was estimated at around 120 to 125°C. Based on the XRD analysis, the clay minerals smectite, chlorite and illite, as well as quartz, calcite, and alunite, were determined as alteration minerals in this region, which represent high temperature environment (>180°C). The obtained data suggest that the water in the Hanle region was likely formed either by the mixing of groundwater and heated fossil seawater, or by the dissolution of evaporite by heated groundwater.

Keywords: hydrothermal alteration, Hanle, Djibouti, Geochemistry

Öz

Bu çalışmada, Hanle Jeotermal Alanının (Cibuti-Doğu Afrika) jeokimyası ve hidrotermal alterasyonuna dayalı olarak alanın jeotermal potansiyelinin araştırılması amaçlanmıştır. Hanle grabenindeki beş içme suyu kuyusundan, bir kaplıcadan ve bir buhar yoğuşmasından alınan sulardan hidrojeokimyasal analizler yapılmıştır (pH, elektrik iletkenliği (EC), SiO_2, Cl, SO_4, HCO_3, F, Na, K, Ca, Mg, Al, Fe, B, As, δD, $\delta^{18}O$). Bu suların doygunlukları ve çeşitli jeotermometreler kullanılarak, rezervuar sıcaklığının yaklaşık 120- 125°C olduğu tahmin edilmiştir. XRD çözümlemelerinde yüksek sıcaklık ortamını (>180°C) temsil eden smektit, klorit ve illit türü kil mineralleri ile kuvars, kalsit ve alunit gibi alterasyon mineralleri belirlenmiştir. Elde edilen veriler, Hanle bölgesindeki suyun ya yeraltı suyu ve ısıtılmış fosil deniz suyunun karışmasıyla ya da ısıtılmış yeraltı suyunun evaporiti çözmesiyle oluşmuş olabileceğini göstermektedir.

Anahtar kelimeler: hidrotermal alterasyon, Hanle, Cibuti, Jeokimya

1 Introduction

Due to an exceptional geodynamic situation, the Afar Depression, a triple junction of the Red Sea, the Gulf of Aden and the East African Rift, where volcanic and tectonic activity has been taking place since 30 Ma, the Republic of Djibouti is characterized by numerous current and past hydrothermal activities [1]. The Italian National Research Council and the French National Center for Scientific Research conducted detailed studies of the area in the 1970s and confirmed the existence of spreading axes, similar to oceanic rifts, in Afar [2]. The landmass of Djibouti consists mainly of volcanic rocks, given the volcanism and extensive tectonism that has occurred there since 25 Ma. The most tectonically active structure in Djibouti is the Assal rift. The series of volcanic rocks that were formed during different phases of volcanic eruption and expansion are the Adolei basalts (25 Ma), Mabla rhyolites (15 Ma), Dalha basalts (9 Ma), Ribta rhyolites (4.25 Ma), Stratoid basalts (3.3 Ma), Gulf of Tad- joura basalts (3.1 Ma), and recent rift basalts (Holocene to present) [3]. Phases of extensional tectonics and related volcanism have also created numerous geothermal systems in Djibouti. The first geothermal exploration in Djibouti was conducted by the French Geological Survey in the 1970s [3]. 23 geothermal sites have been recognized in the Republic of Djibouti. The Hanle study area (Figure 1) is one of the top 5 most-valued sites and is located close to the Gagade region of the Great East African Rift, which is currently active and opening at a rate of 10 to 15 mm/year [4]. The aim of this study is to reveal the energy potential of the Hanle geothermal field and to integrate it into Djibouti's economy. In this context, the study was to highlight the relationships between the heat source, the reservoir rock and the cap rock, and to identify the zones of high-temperature fluid production as a function of the permeability of the reservoir rock.

2 Geological and hydrogeological setting

The study area is a plateau located between the Hanle Plain and the Gaggade Plain in the NW-SE direction and its altitude varies between 300~500 m. In the Hanle Plateau, the basaltic lava Afar Stratoid Series (Figure 1) can be divided into 3 layers according to the state of lithofacies: the lower basalt layer, the middle basalt layer and the upper basalt layer. Between basalt layers, aqueous sedimentary tuff can be found. In the northern part of the study area, a thick layer of rhyolite lava is distributed under the basalt layer.

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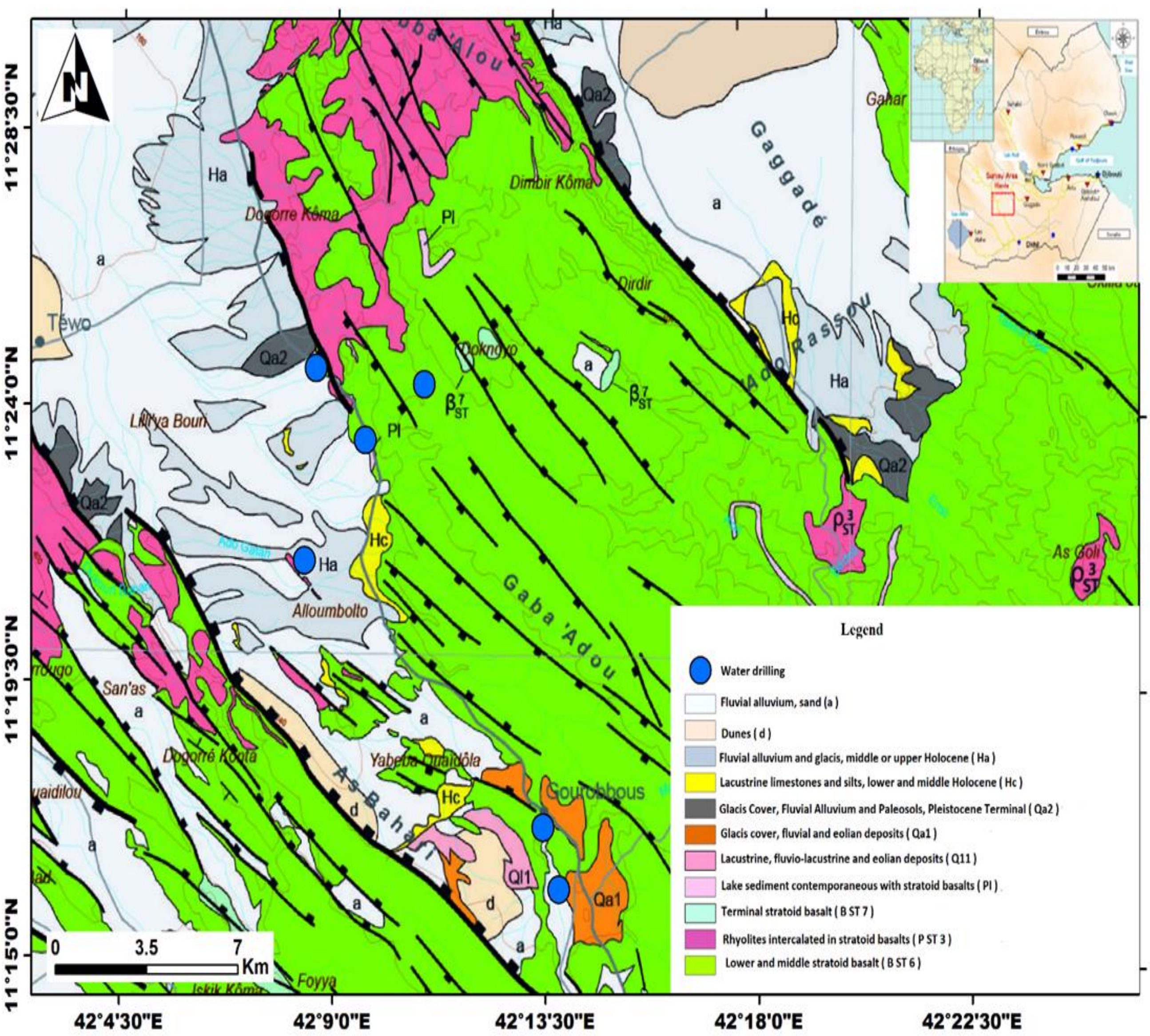

Figure 1. Geological characteristics of the study area [2].

In contrast, marine sediments, lake sediments, river sediments, and Aeolian sediments formed in the Pliocene to Pleistocene were deposited in the Hanle Plain and the Gaggade Plain.

Within the study area, many successive faults or fractured systems were formed in the NW-SE direction. Most of the faults are normal faults that lie in a NE-direction. These faults form fault scarps with a height difference of about 5~20 m and are sequentially distributed on the Hanle Plateau (Jica 2014 unpublished report). Most of these faults have caused displacement of the middle basalt layer on the plateau. Fieldwork confirmed the presence of a diffuse calcite hydrothermal vertical and accompanying altered minerals.

Djibouti aquifer systems; basalts and rhyolites just beneath the alluviums form shallow local aquifers. Stratoid volcanic rocks, where geothermal circulation occurs, mainly form the reservoir rock. Cretaceous sedimentary rocks, which occasionally cover the volcanic rocks, represent aquitard and aquiclud environments.

3 Materials and methods

Samples were collected from steam condensate, from hot spring, and water wells (groundwater) in January and September to interpret a geochemical structure related to a geothermal system in the Hanle area (Figure 2). The samples were analyzed for chemical and stable isotopic composition in Japan (University of Kyushu) and in France (University of Corsica). The analysis methods and parameters measured are summarized in Table 1 below.

Table 1. Sample treatment and analytical methods for geothermal water.

Phase	Treatment	Specification	To determine	Analytical method
Liquid	None, amber glass bottle withairtight stopper	Ru	pH, conductivity, CO_2, H_2S *(In situ)*	Potentiometry, Titrimetry
	Dilution; 50 mL of sample +50 mL of distilled, deionizedwater	Rd (1:1)	SiO_2 if > 100 ppm	Spectroscopy withammonium molybdate
	Filtration	Fu	F, Cl, Br, SO_4, B	Ion chromatography, Spectros-copy
	Filtration: 0.8 mL of HNO_3added to 200 mL sample	Fa	Na, K, Mg, Ca, Fe	Atomic absorptionspectroscopy
	Filtration; 2 mL of 0.2 MZnAc$_2$ + 98 mL of sample	Fp	SO_4	Ion chromatography
	Filtration	Fu	^{2}H, ^{18}O	Mass spectrometry

In the previous geochemical study conducted by JICA around the Hanle lava plateau, several rock samples were analyzed in the Japanese laboratory to understand the mineralogy, texture, and structure of the rocks, providing crucial information on the geological formation of the region.

To identify primary and secondary minerals as well as hydrothermal alteration minerals, samples of rocks collected from the study area were analyzed in the geological laboratory of Kyushu University. Powdered bulk samples were prepared in the laboratory for XRD analysis. A ground powder sample was prepared, with great care taken to avoid contamination, before the XRD analysis can be conducted. To prepare the bulk sample, the rock samples were crushed into small pieces and dried in an oven at 45 °C for 1 d to remove moisture from them. The sample was then crushed into a powder. Finally, the powdered samples were compressed into a thin film on a metal plate to allow the use of XRD to properly analyze the altered minerals.

4 Results and discussion

4.1 Hydrogeochemical results

Analyzed items for water samples (hot spring water, groundwater, and steam condensate) are as – pH, electric conductivity (EC), SiO_2, Cl, SO_4, HCO_3, F, Na, K, Ca, Mg, Al, Fe, B, As, δD, $\delta^{18}O$ (Table 2).

Table 2. Results of analysis for water samples.

Name	Type	Seasons	Ca^{++} (mg/l)	Mg^{++} (mg/l)	Na^{+} (mg/l)	K^{+} (mg/l)	Cl^{-} (mg/l)	SO_4^{--} (mg/l)	HCO_3^{-} (mg/l)	T°C	pH	EC (mS/m)	$\delta^{18}O$ (‰)	δD (‰)
Dirdir	Water well	Rainy	47	4.8	862	3.6	852	589	198	28.8	7.5	4170	-2.5	-21
Kori	Hot spring	Rainy	50	4.0	724	20	1000	224	169	48.0	7.8	3780	-0.4	-5
Garrabeyis	Steam cond.	Rainy	79.32	29.14	264.74	3.94	362.82	267.51	69.51	58.4	7.9	1968	-8.5	-51
Cheiksabir	Water well	Rainy	21	24.4	201	5.70	108	160	306	38.5	7.9	1279	-0.6	-
Goros	Water well	Rainy	24	3	110	2	39	55	232	34.8	8.1	711	0.1	2
Garabbayis	Dug well	Dry	36	3.4	156	6.8	43	256	104	32.6	8.3	1037	1.1	9
Kori	Hot spring	Dry	29	3.6	262	14	273	176	112	53.8	8	1617	-	-1
Chek Sabir	Water well	Dry	83.95	18.94	142.55	4.46	87.39	317.03	204.74	42.5	7.5	965	-	-
Garabbayis	Steam cond.	Dry	0.04	0.01	0	0	0.04	0.73	153	99.7	5.8	36	-	-
Gorabous	Water well	Dry	132.47	0.00	381.18	17.46	199.50	595.34	311.83	35.8	8.29	1812	-	-
Kouxikooma	Water well	Dry	141.26	24.71	97.39	4.27	97.36	273.02	212.65	38.0	7.4	972	-	-
Garrabeyis	Rainwater	Dry	42.00	0.82	66.08	5.45	13.79	73.91	185.71	31.0	8.6	406	-	-

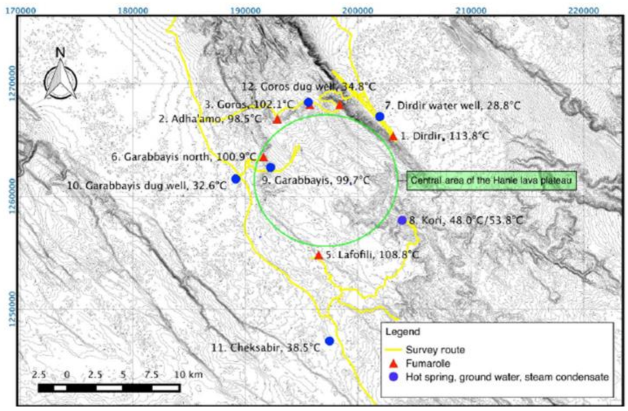

Figure 2. Map of sample locations.

Very little rainfall reduces seasonal differences during the sampling period. The relative contents of the main anions, Cl, SO_4 and HCO_3, are shown in Figure 3. The original components originate from subduction zones along the Pacific coast [5]; these are mature, peripheral, steam-heated and volcanic waters.

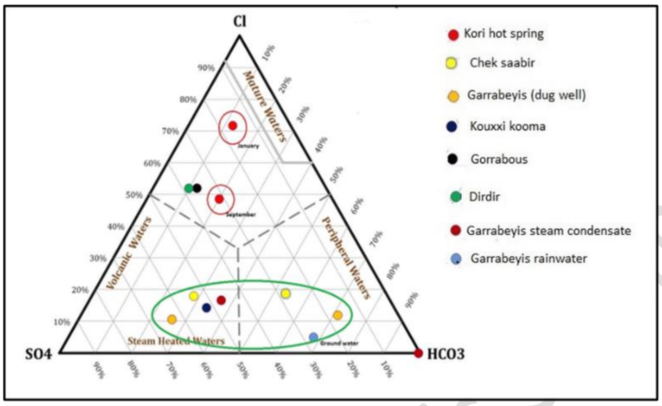

Figure 3. Cl - SO_4 - HCO_3 diagram of study area.

According to the Piper diagram, which is used for determining the relationships between the various dissolved constituents in water and for identification of ionic types and hydrochemical facies of water, the waters in the study area are distributed in different fields over the two periods (Figure 4).

On the diamond shaped central field of the Piper diagram (Figure 4A), the samples collected during the rainy season plot in five fields (2, 3, 4, 7 and 9). All samples plot in the field 2 and indicate that in all samples alkali metals (Na+K) exceed alkaline earths (Ca+Mg). One of the samples plots in the field 3 and indicate weak acids exceed strong acids. The remaining samples plot in the field 4 and indicate strong acids exceed weak acids in these samples. Five samples plot in the field 7, suggesting that they are sodium chloride type, but one samples plot in the field 9 represented by mixed type water. Cation abundance-wise, the rainy season samples are sodium and Potassium type waters. On the other hand, anion abundance-wise, they are mainly chloride type, but other types are possible (e.g. mixed type, sulphate type etc.).

The hot season samples are similar to those of the rainy season samples, except for two samples in the field 1 (e.g., alkaline earths exceed alkali metals and 5 (e.g., magnesium bicarbonate type), based on the diamond shaped central field of the Piper diagram (Figure 4B). Cation abundance-wise, the hot season samples are mainly sodium and potassium type waters, but calcium types are also possible. On the other hand, anion abundance-wise, they are mainly sulphate type, but other types are possible (e.g. mixed type, chloride type etc.).

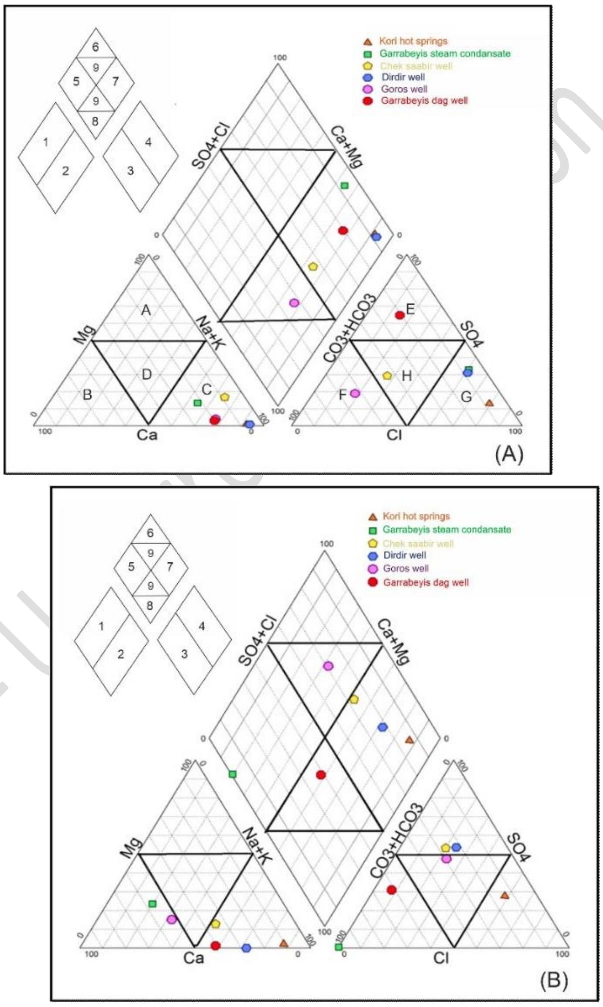

Figure 4. Piper diagram of the study area (A- Rainy season, B- Hot season). A – Magnesium type; B – Calcium type; C - Sodium and Potassium type ; D - No dominant type ; E - Sulphate type; F- Bicarbonate type ; G – Chloride type; H- No dominant type; 1 – Alkaline earths exceed alkali metals; 2 – Alkali metals exceed alkaline earths; 3 – Weak acids exceed strong acids; 4 – Strong acids exceed weak acids; 5 Magnesium bicarbonate type; 6 – Calcium chloride type; 7 – Sodium chloride type; 8 – Sodium bicarbonate type; 9 – Mixed type.

In January Kori and Dirdir samples show relatively large content of Cl. Much larger content of Cl is seen at the coastal areas and near Lac Asal in Djibouti. Absolute concentration of Cl tends to be very high at the coastal areas and near Lac Asal, and moderate in the Hanle plane (Garrabeyis with 13.79) and lava plateau. The origin of such content of Cl seems to be modern seawater for the coastal and Lac Asal areas, and to be fossil seawater or it's evaporate captured in a formation during a past marine transgression.

To examine water-rock interaction from the chemical composition of the Kori hot spring, relative contents of Na, K, and Mg [6] are illustrated in Figure 5. The diagram indicates that the Kori hot spring in January is partially equilibrated with rock, which means that a subsurface region around the Kori spring has temperature conditions under which water–rock interaction proceeds to some extent. On the other hand, in September the Kori hot spring is plotted in immature waters region out of the partial equilibrium. As mentioned above, this is probably because that the Kori hot spring water was diluted more with groundwater in September than in January.

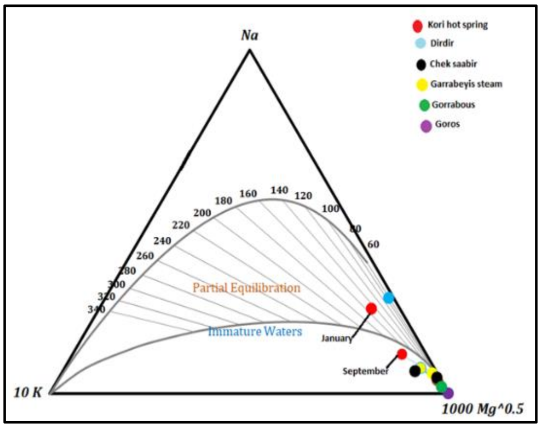

Figure 5. Relative Na, K, and Mg contents of water samples.

4.2. Geothermometers

Seven geothermal equations were used to estimate the subsurface temperature (Table 3): three for Na-K, one for chalcedony, one for quartz, one for K-Mg and one for Na-K-Ca. In the Hanle area, weak alteration of the rock is observed, for which the chalcedony geothermometer was chosen. The chalcedony result indicates that the hot spring aquifer has a temperature of about 125°C (Table 3), which is shallower than the geothermal reservoir.

4.3 Isotope

Relationship between hydrogen and oxygen isotopic ratios of water samples of hot springs, water wells, and the fumarole at Garabbayis (steam condensate) are shown in Figure 5. Most of the samples are plotted on and close to a line with a slope of 8 except for the steam condensate. The condensate is plotted away from the line and the isotopic ratio is significantly lower than that of the hot springs and water wells. This is due to isotope fractionation during boiling water. Due to the climatic characteristics of Djibouti, which is located on the ocean coast, the low rainfall, high temperature and evaporation cause an excess of Oxygen-18 and a low Deuterium exchange.

In that process, vapor becomes enriched in light isotopes, thus the isotopic ratio becomes low. Figure 6 shows a shift of the isotopic ratio in Kori hot spring between January and September; the isotopic ratio approached those of groundwater (water wells). This shift probably means more mixing of groundwater with Kori hot spring in September as suggested above by a major anion relative contents and relationship of concentration between Na and Cl.

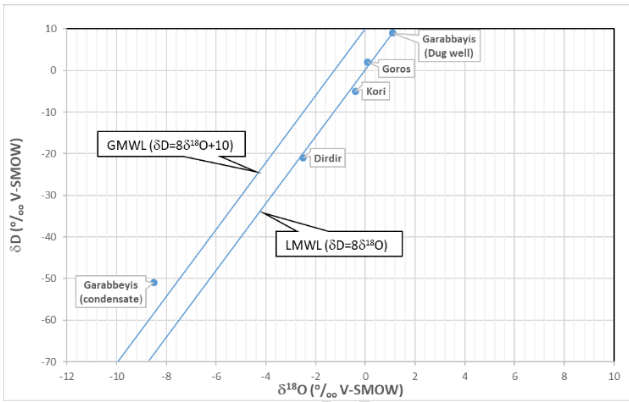

Figure 6. Relationship between hydrogen and oxygen isotopic ratios of the Hanle Geothermal Area (GMWL; Global Meteoric Water Line-$\delta D=8\delta^{18}O+10$, LMWL; Local Meteoric Water Line-$\delta D=8\delta^{18}O$).

4.4 Saturation index

While most geothermal waters are saturated with minerals such as calcite, dolomite and aragonite [11], Hanle Geothermal waters are saturated with minerals such as anhydrite, gypsum, fluorite and halite.

In order to estimate the temperature of the geothermal reservoirs in the Hanle zone, we calculated the saturation index of the various water boreholes using Phreeqc software. The saturation index results obtained are plotted below in Figure 7.

Using Phreeqc software, we were able to determine the saturation index of each sample up to a temperature of 160°C. The highest temperature was recorded in the Garrabeyis borehole at approximately 120 °C. Temperatures in other boreholes ranged from 40°C to 80 °C.

4.5 Petrographic observations

Observation of rock thin sections was conducted on polarized microscope to identify rock-forming minerals, textures, alteration minerals and their characteristics. The identified primary minerals are olivine, clinopyroxene, plagioclase and opaque minerals (Figure 8A), whereas alteration minerals are mainly calcite and quartz (Figure 8B) in most of the thin sections.

Calcite and quartz are common and widespread vein and vesicle filling minerals, pointing to the carbonation and silicification.

Table 3. Results of calculation of geochemical geothermometers for the Kori hot spring.

Sample	Seasons	Manifestation	Temperature measured (°C)	Geothermometers results (°C)						
				Quartz [7]	Chalcedony [8]	Na-K [7]	Na-K [9]	Na-K [6]	K-Mg [6]	Na-K-Ca [10]
Kori	Rainy	Hot spring	48	142	125	115	127	147	94	143
Kori	Dry	Hot spring	53.8	120	110	153	169	187	86	153

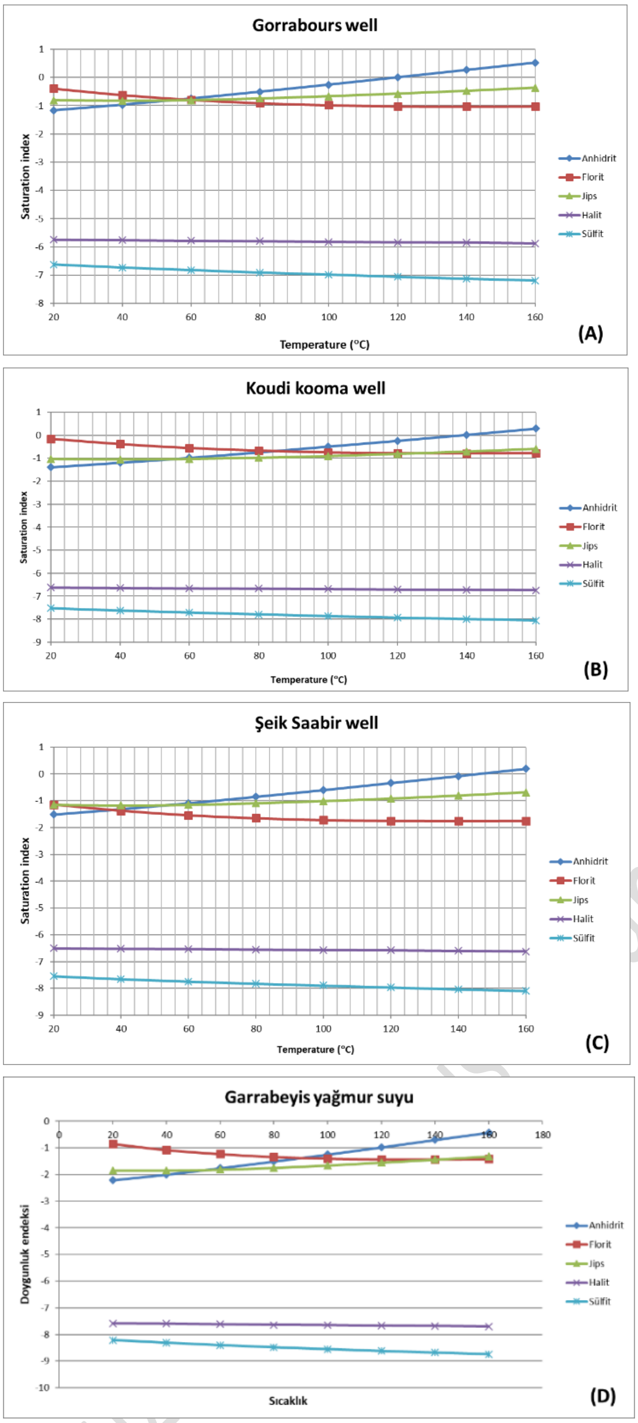

Figure 7. Temperature versus SI diagrams as representatives of thermal wells and springs. (A-gorrabous well, B- Koudi kooma well, C- Chek saabir well, D- Garrabeyis well).

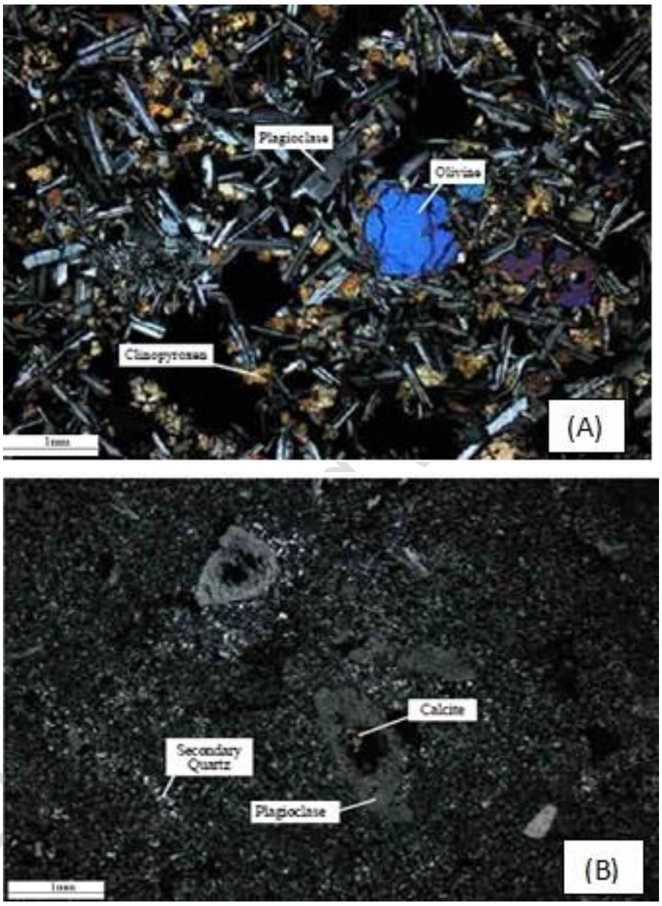

Figure 8. Appearances of minerals on the polarized microscope (A- Rhyolit, B- Basalt, C- Basalt, D- Basalt).

4.6 XRD results

The results show that the alteration minerals in this area are mainly quartz, calcite, albite, and the clay minerals chlorite, smectite and illite (Figure 9-10). Quartz occurs either as an alteration product of opal or chalcedony or as a vesicle or vein filling mineral [12]. It (quartz) is commonly associated with epidote, prehnite, pyrite and calcite [13]. Epidote is a common and abundant mineral formed in geothermal systems. Its presence in significant quantities indicates temperatures above 200°C (Figure 11).

Clay minerals are widely used as temperature indicators in geothermal exploration; they are the best tool for this purpose [14]. Smectite is the clay mineral with the lowest formation temperature; it is formed directly by the alteration of glass or primary minerals such as olivine in water-rock interactions and precipitates in cavities and veins. Smectite is an indicator of temperatures below 200°C. Chlorite occurs both as a replacement for primary minerals in rocks and as a void fill; it is an indicator of temperatures above 230 °C [15].

These results show that the presence of clay minerals such as smectite indicate that the hydrothermal alteration in this region is acidic to neutral. However, the samples containing the clay minerals chlorite, calcite, and illite indicate that they are neutral to alkaline. The presence of calcite, smectite and chlorite (Figure 11) indicates high temperatures.

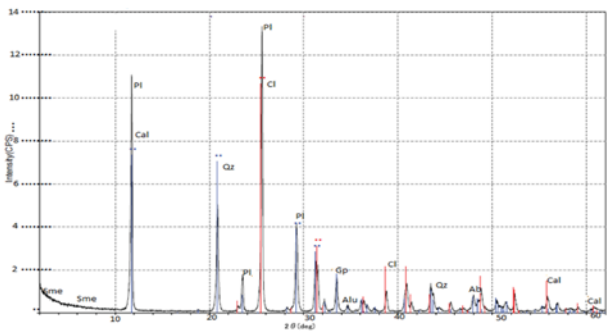

Figure 9. (H1): X-ray diffraction patterns for the bulk sample (pl: plagioclase, Qz: quartz, cal: calcite, gp: gypsum, Ab: albite, Anh: Anhydrite, Alu: Alunite, Sme: smectite, Chl: chlorite).

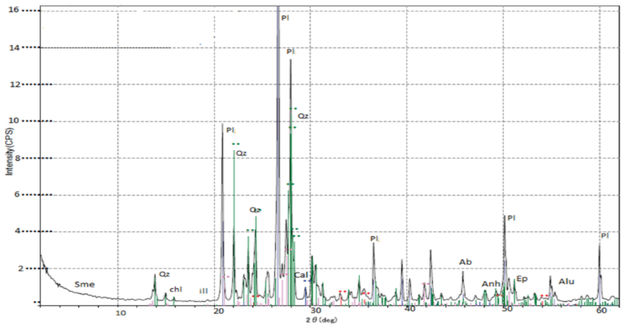

Figure 10. (H2): X-ray diffraction patterns for the bulk sample (pl: plagioclase, Qz: quartz, cal: calcite, gp: gypsum, Ab: albite, Anh: Anhydrite Alu: Alunite, Ep: Epidote).

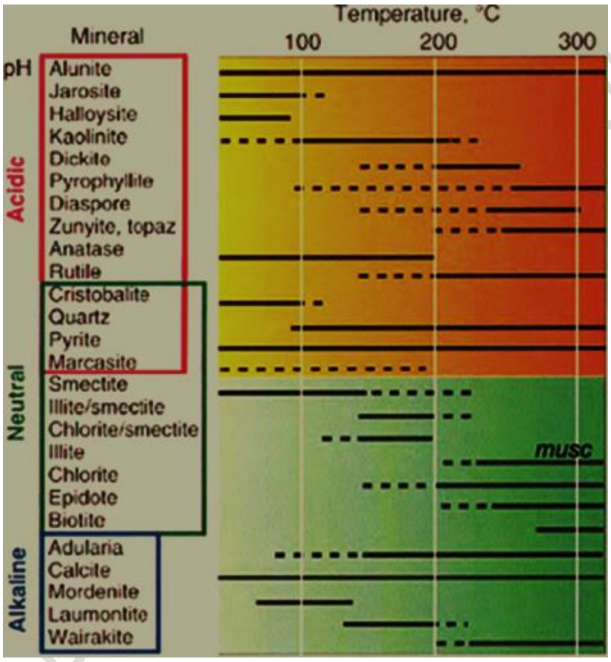

Figure 11. Variation in mineral stability with temperature at quartz solubility (dashed line for stability at amorphous silica solubility), Modified from [16].

5 Conclusions

Having established the chemical facies of the study area, we can see that the various water points in the Hanle region are not intensely mineralized. Using the chemical compositions of the hot springs, reservoir temperature was estimated to be 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. The reservoir temperature was also estimated with PHREEQC and gave 120 degrees, almost the same temperature as we had obtained with the geothermometer at the Kori hot spring.

XRD analysis shows that the alteration minerals in this area are mainly quartz, calcite, albite, and the clay minerals smectite, chlorite and illite. This composition results in the formation of hydrothermally altered minerals, some of which are known to occur in specific and stable temperature regimes. The clay represents a transition to a high temperature environment as evidenced by the presence of high temperature hydrothermal alteration minerals such as quartz (>180°C) and epidote (~250°C). Therefore, the results of the XRD analyses provide a good indication of geothermal system in the Hanle area.

6 Author contribution statements

In the scope of this study, Author 1 in the formation of the idea, the literature review, coding and performing the experiments and writing the draft manuscript; Author 2 in the formation of the idea, examination of the results, the spelling and checking the article in terms of content were contributed.

7 Ethic committee approval and conflict of interest statement

"There is no need to obtain permission from the ethics committee for the article prepared."

"There is no conflict of interest with any person/institution in the article prepared."

8 References

[1] Khaireh A, Fouad A. "Geothermal Development in Djibouti Republic: A Country Report". *Proceedings 4th African Rift Geothermal Conference*, Nairobi, Kenya, 21-23 November 2012.

[2] Geoffroy L, Le Gall B, Daoud MA, Jalludin M. "Flip-flop detachment tectonics at nascent passive margins in SE Afar". *Journal of the Geological Society* 171 (5), 689-694, 2014.

[3] Corti G, Bastow ID, Keir D, Pagli, C. "Rift-related morphology of the Afar Depression". *in Landscapes and Landforms of Ethiopia, ed. P. Billi, (Dordrecht: Springer Science Business Media),* 251-274, 2015.

[4] Geoffroy L, Bernard Le G, Mohamed D. "Plate break-up geometry in SE-Afar". *EGU General Assembly Conference Abstracts*. Vienna, Austria, 27 April – 02 May 2014.

[5] Giggenbach WF, Matsuo S. "Evaluation of results from Second and Third IAVCEI field workshops on volcanic gases, Mt Usu, Japan, and White Island, New Zealand". *Applied Geochemistry* 6, (2) 125-141. 1991.

[6] Giggenbach WF, Minissale AA, Scandiffio G. "Isotopic and chemical assessment of geothermal potential of the Colli Albani area, Latium region, Italy". *Applied Geochemistry*, 3 (5) 475-486, 1988.

[7] Arnórsson S. "Isotopic and chemical techniques in geothermal exploration, development and use. Sampling methods, data handling, and interpretation". Introductory course, GTP. IS-108, Reykjavik, Iceland, p. 199, 2000.

[8] Arnórsson S, Gunnlaugsson E, Svavarsson H. "The chemistry of geothermal waters in Iceland. III. Chemical geothermometry in geothermal investigations". *Geochimica et Cosmochimica Acta* 47 (3), 567-577, 1983.

[9] Fournier RO, Potter RW. "Magnesium correction to the Na-K-Ca chemical geothermometer". *Geochimica et Cosmochimica Acta*, 43 (9), 1543-1550, 1979.

[10] Fournier RO, Truesdell AH. "An empirical Na-K-Ca geothermometer for natural waters". *Geochimica et Cosmochimica Acta,* 37 (5), 1255-1275, 1973.

[11] Balaban TÖ, Akın H, Tarcan G, Gemici Ü, Çolak M, Karamanderesi İH. "Hydrogeochemical study of the Gümüşköy spa (Aydın) and its vicinity". *Pamukkale University Journal of Engineering Sciences,* 22(6), 553-558, 2016.

[12] Mehegan JM, Robinson PT, Delaney JR. "Secondary mineralization and hydrothermal alteration in the Reydarfjordur drill core, eastern Iceland". *Journal of Geophysical Research: Solid Earth,* 87 (B8), 6511-6524, 1982.

[13] Hedenquist JW, Arribas AR, Eliseo GU. "Exploration for epithermal gold deposits". *In: S.G. Hagemann and P.E. Brown (Editors), Gold in 2000: Society of Economic Geology Special Publication,* 13, 245-277, 2000.

[14] Kristmannsdóttir H. "Alteration of basaltic rocks by hydrothermal-activity at 100-300 C". *Developments in Sedimentology,* 27, 359-367, 1979.

[15] Stakes DS, O'Neil JR. "Mineralogy and stable isotope geochemistry of hydrothermally altered oceanic rocks". *Earth and Planetary Science Letters,* 57 (2), 285-304, 1982.

[16] Randive K, Chaudhary S, Dandekar S, Deshmukh K. "Characterization and genesis of the chalcedony occurring within the Deccan lava flows of the LIT hill, Nagpur, India". *Journal of Earth System Science,* 128, 1-12, 2019.