Proceedings World Geothermal Congress 2020+1
Reykjavik, Iceland, April - October 2021

Geochemical Study of Lake Abbe Geothermal Field, Djibouti

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Keywords: Djibouti, Lake Abbe, Hydrochemistry, Thermal water, Geothermometry

ABSTRACT

The Lake Abbe geothermal field is located in the south-western region of the Republic of Djibouti, on the border with Ethiopia. It is one of the thirteen potential geothermal sites identified in Djibouti. This area is dominated by stratoid basaltic rock and is marked by hydrothermal activities, which are manifested by hot springs with surface temperatures of more than 90°C; fumaroles and travertines are also found in this area. Hot springs and fumaroles were sampled and analyzed. Geochemical data is interpreted in this report to estimate the reservoir temperatures and properties. The different geothermometers estimate the temperature of the reservoir to be in the range between 107-160°C. Hydrothermal data shows that the thermal waters have a high concentration of chloride, which classifies them as volcanic waters, and that these waters are equilibrated with the rock. The stable isotopic (δD and $\delta^{18}O$) composition and Cl/B ratio were used to determine the origin of the water. The thermal waters are local meteoric waters from the same sources and they are not mixed with Lake Abbe water. The estimated reservoir temperatures suggest that the Lake Abbe geothermal area is a medium-temperature geothermal system.

1. INTRODUCTION

The purpose of this report is to interpret chemical data of thermal waters and gas from Lake Abbe prospect,Djibouti. The Republic of Djibouti is located in the Horn of Africa in the East Africa rift system 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. Djibouti has thirteen geothermal areas of interest, including the study area, which has been identified as being promising in terms of potential electricity generation utilizing geothermal fluids.

The Lake Abbe zone is located in the south western region of the country (Figure 1), at the border of Ethiopia. It lies in the Afar depression and the lake is connected to the Awash River. Fumaroles and hot springs, mainly alkaline chloride, are visible over a large area of more than 100 km^2 with the surface temperatures of more than 90°C, and many spots with temperatures between 100°-105°C. This observation suggests that in the Lake Abbe zone, an important thermal anomaly exists, representing a potential geothermal reservoir.

The main objectives of the present study are to interpret the water and gas 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 by interpreting the chloride to boron ratio and the stable isotopic composition (oxygen and deuterium).

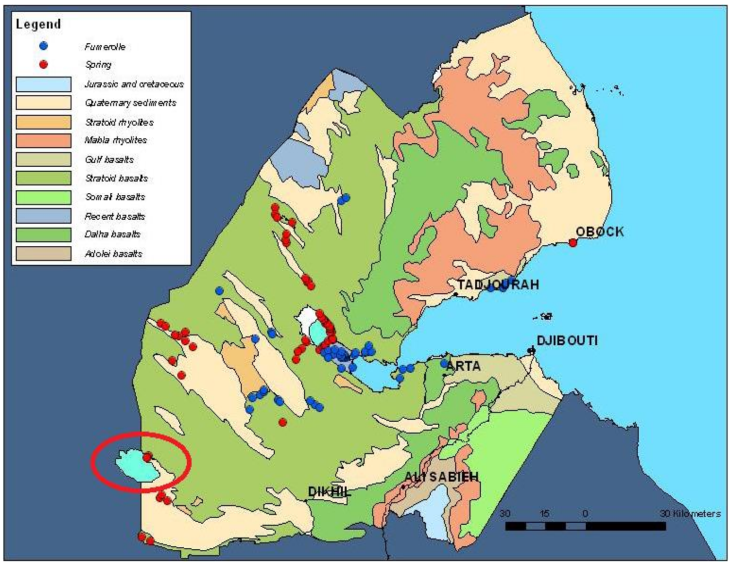

Figure 1: Geological map of Djibouti (CERD).

2. METHODS

2.1 Sampling of Springs and Fumaroles

2.1.1 Sampling of Springs

When collecting samples from hot springs, it is good if the water is free flowing from the sampling spot. If not, a sampling pump is needed. The water temperature and discharge rate are recorded. An untreated sample is collected in an air-tight bottle for pH, CO_2, H_2S and conductivity measurements. If the subsurface temperature is assumed to be high, the sample is diluted with deionized water, for analysis of SiO_2, to produce a dilutedSiO_2concentration of 30 to 100 ppm. A filtered sample is collected for anions, and a filtered and acidified sample is collected for cation analysis. The filters are a 0.45 μm pore size membrane, and the acid used is Suprapur HNO_3. To analyze SO_4, the sample is filtered and sulfide precipitated with zinc acetate ($Zn(CH_3COO)_2$). For the analysis of stable isotopes, the sample is filtered and collected in an airtight 60 mL glass bottle. The various sub-samples collected are described in detail in the Table 1.

Table 1: 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

2.1.2 Sampling of Fumaroles

The selection of fumaroles for sampling is not as straightforward as that of hot springs. It is generally best to sample small outlets which discharge steam at a considerable flowrate in areas of the most intense acid surface alteration. Before the sampling, a NaOH solution should be prepared in the laboratory and put in a double port bottle which is then evacuated. The CO_2 and H_2S present in the steam dissolve quantitatively in the alkaline solution whereas the other gases remain in the headspace of the bottle. Samples of condensed steam are also collected. An untreated fraction is collected for Cl, B and Na analyses, and a fraction for analyses of stable isotopes of oxygen and hydrogen is collected in an airtight amber glass bottle (Table 1).

2.2 Chemical Analysis

Parameters like conductivity and temperature of the water are measured in situ while the pH and concentration of CO_2 and H_2S in samples are analyzed in a field laboratory the same day. The major chemical constituents in water samples are analyzed in the geochemical laboratory using the analytical methods shown in the Table 1.

3. RESULTS AND DISCUSSIONS

In this study, eight hot springs, one cold groundwater and one fumarole were collected (Figure2) and analyzed. The major, minor and trace elements of these waters are reported in Table 2. The temperature of the geothermal water samples of Lake Abbe ranged from 94.2° to 99.8°C. The conductivity of these water ranges between 3140-7210 µS/cm.

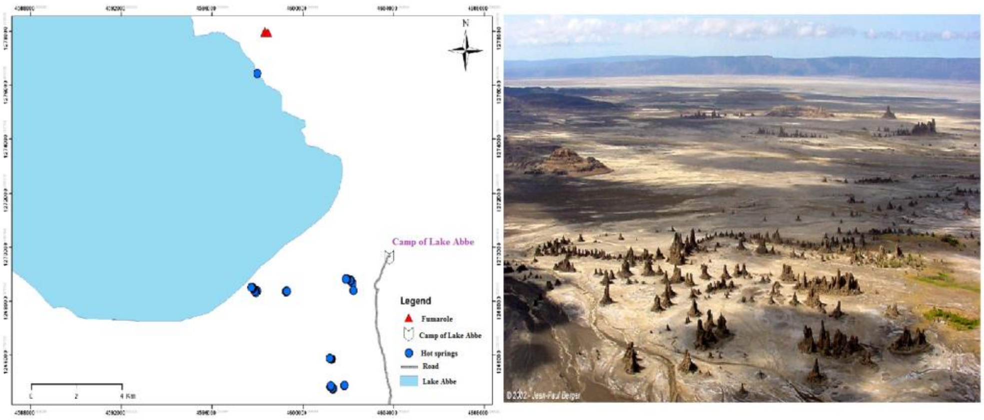

Figure 2: Location map of geothermal manifestations (left). Travertine chimneys (right).

Table2: Chemical data of springs in Lake Abbe geothermal area.

Analyte	Unit	Abbe-01	Abbe-02	Abbe-03	Abbe-04	Abbe-05	Abbe-06	Abbe-07	Abbe-12	Groundwater	Lake Abbé
Temp	°C	96,9	99,6	99,8	99,8	94,2	95,8	99,5	99,5	34	
EC/Temp	µS/cm/°C	5580/34,1	5360/34,9	7210/30,1	3580/38,3	3380/38,4	3180/32,9	3140/32,8	5410/34,4	5190/32,3	-
B	mg/l	1,47	1,39	2,06	1,01	0,99	0,98	0,95	1,57	2,25	100
Br	mg/l	7,21	7,16	9,62	4,51	4,38	4,26	4,03	7,38	5,26	209
Ca	mg/l	225	217	262	177	173	161	157	223	3,87	-
Cl	mg/l	1620	1600	2170	935	912	863	835	1620	1040	39200
CO_2	mg/l	20,8	25,1	29,2	18	16,5	20,5	17,6	22,4	572	
F	mg/l	0,94	1,15	0,97	0,85	0,82	0,83	0,84	1,21	5,26	138
Fe	mg/l	0,03	0,03	0,04	0,03	0,02	0,03	0,02	0,04	0,05	-
H_2S	mg/l	0,02	0,01	0,03	0,03	0,03	0,02	0,04	0,03	0,04	-
K	mg/l	28,3	30,5	35,4	15,7	15,5	15	14,7	25,8	22,8	-
Mg	mg/l	0,18	0,38	0,51	0,06	0,05	0,05	0,08	0,17	2,45	-
Na	mg/l	950	950	1310	567	558	537	527	960	1280	-
SiO_2	mg/l	118	120	104	100	97	100	103	125	40,5	-
SO_4	mg/l	328	325	426	319	308	319	308	322	573	19300
TDS	mg/l	3570	3630	4660	2370	2320	2200	2170	3550	3470	-
HCO_3	mg/l	28,84	34,80	40,48	24,95	22,88	28,42	24,40	31,05	793,00	-
δD	‰VSMOW	-	-25,55	-23,1	-27,29	-	-	-26,62	-	4,94	58,63
$\delta^{18}O$	‰VSMOW	-	-3,17	-3,26	-3,2	-	-	-3,22	-	1,38	9,12

3.1 Cl-SO_4-HCO_3Ternary Diagram

This diagram classifies geothermal waters using the major anion concentrations (chlorides, sulphates and bicarbonates) (Giggenbach, 1988) and also helps distinguishing the waters as mature, peripheral, volcanic or steam-heated waters. On the triangular diagram Cl-SO_4-HCO_3 in Figure 3, thermal waters are near to the chloride corner but not in the field of mature geothermal waters. This part of the diagram represents waters of volcanic origin. From this diagram, the thermal samples plot quite close to the lake water composition. It can be interpreted that these thermal waters are probably volcanic waters, while groundwater is cold water and its location in this figure indicates that this water is mixed water.

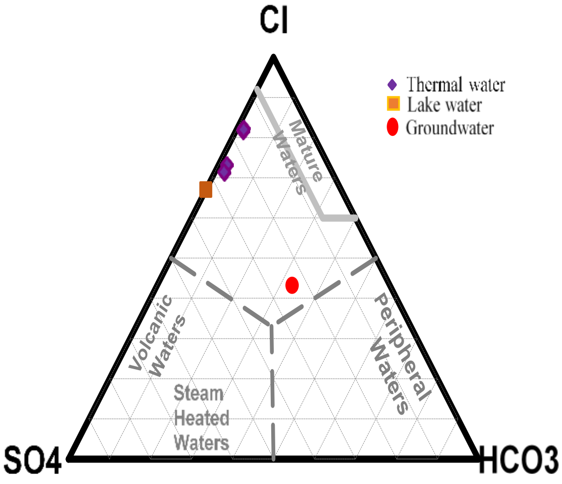

Figure 3: Cl-SO_4-HCO_3 ternary diagram for Lake Abbe water samples.

3.2 Na-K-Mg Ternary Diagram

The ternary diagram of Na-K-Mg shown in Figure 3 was developed by Giggenbach (1988). It is used to estimate the reservoir temperature and to select the waters most suitable for geothermometry by recognizing the fluid maturity of waters which have attained equilibrium with the host rock. A similar deduction is also underscored by Fournier (1990). Data points that plot on the full equilibrium in the diagram indicate that water-rock equilibrium has been attained. Plotting on the partial equilibrium indicates either a mineral that has dissolved but has not attained equilibrium or geothermal water that has mixed with dilute unequilibrated cold water. Immature water indicates initial dissolution of minerals before equilibrium reaction begins.

Figure 4 shows that the thermal water samples are fully equilibrated or close to equilibrium, whereas the groundwater sample is only partially equilibrated. It is normal that this groundwater is not at equilibrium because at low temperatures the reactions between the water and the rock are very slow.

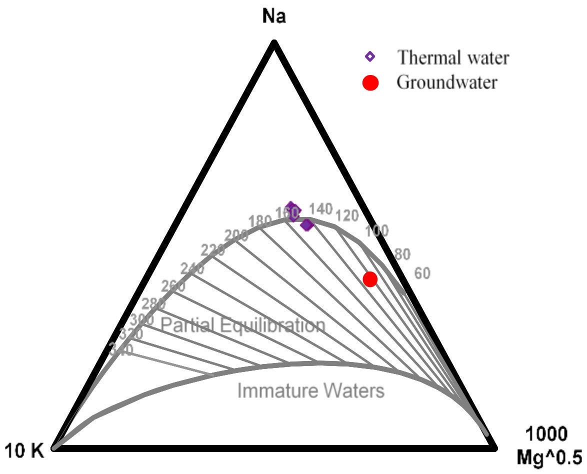

Figure 4: Na-K-Mg ternary diagram for Lake Abbe water samples.

3.3 Silica and CationGeothermometers

In this paper, nine geothermometers equations were used (Table 3): three for quartz, three for Na-K, two for chalcedony, and one Na-K-Ca. Among the six quartz geothermometers, three are chosen because the samples were collected at the surface, thus the geothermal fluid has boiled down to 100°C: equations 2, 4 and 6. For the Na/K geothermometer also three equations were chosen: equations 12, 14 and 16. They are applied to predict subsurface temperatures of the geothermal water from Lake Abbe. All the thermal water samples lie in the temperature range 121°-145°C for quartz, 107°-125°C for chalcedony, 91°-124°C for Na-K and 84-115°C for Na-K-Ca. The average temperature calculated was 133°C, 114°C, 109°C and 97°C for quartz, chalcedony, Na-K and Na-K-Ca respectively. The Na-K geothermometer temperatures were high while the Na-K-Ca geothermometer gave low temperatures.

Table 3: Calculated values for 9 equations for solute geothermometers temperatures (in °C) for Lake Abbe, Djibouti

	Quartz			Na-K			Chalcedony		Na-K-Ca
Name	$T_{qz,1}$	$T_{qz,2}$	$T_{qz,3}$	$T_{Na\text{-}K,4}$	$T_{Na\text{-}K,5}$	$T_{Na\text{-}K,6}$	$T_{ch,7}$	$T_{ch,8}$	$T_{Na\text{-}K\text{-}Ca,9}$
Abbe-01	141	142	131	97	120	119	121	119	106
Abbe-02	141	143	132	102	124	123	122	120	110
Abbe-03	135	136	124	91	115	114	113	111	115
Abbe-04	133	134	122	93	116	115	110	109	85
Abbe-05	131	133	121	93	116	115	109	107	85
Abbe-06	133	134	122	93	116	116	110	109	85
Abbe-07	134	135	124	93	116	115	112	111	84
Abbe-12	143	145	134	91	114	114	125	122	103
Abbe-14	94	93	80	67	93	94	62	64	239

(1) Fournier, 1977 (25-250°C); (2) Fournier and Potter, 1982 (25-900°C); (3) Arnórsson, 2000 (0-350°C); (4) Arnórsson et al., 1983 (25-250°C), (5) Nieva and Nieva, 1987, (6) Arnórsson et al., 1998 (0-350°C), (7) Fournier, 1977 (0-250°C), (8) Arnórsson, 2000.

Figure 5 shows comparison plots of calculated temperature results obtained from nine different equations of geothermometers for Lake Abbe. In this area, the silica geothermometers yield temperatures less than about 180°C. Thus, chalcedony appears to control dissolved silica concentrations in the Lake Abbe area. The equilibrium between dissolved silica and quartz is very slow at low temperature. The low value of Na-K-Ca geothermometer (Abbe-04, Abbe-05, Abbe-06 and Abbe-07) is due to the calcium loss (see Table 2 for the Ca values) caused by boiling of water which leads the precipitation of aragonite, confirmed by the travertine deposit. The low temperature reservoir may be explained by greater meteoric recharge or greater heat conduction due to shallow reservoir depths.

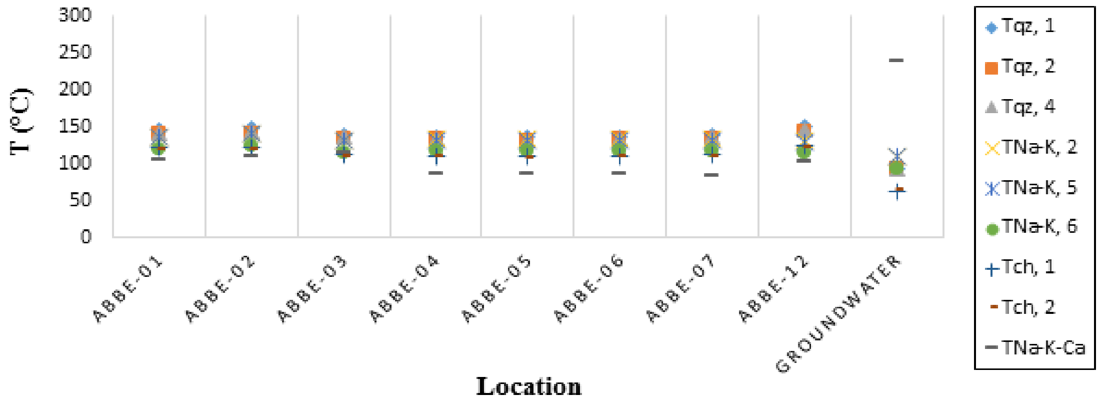

Figure 5: Calculated temperature results obtained with silica geothermometry.

3.4 Gas

The following gases are invariably present in geothermal discharges from both natural features and wells: CO_2, H_2S, N_2, H_2, CH_4, and NH_3. So, it is important to know the behavior of these geothermal gases (Table 4).

Table4: Chemical composition of fumarole in Lake Abbe geothermal area. The concentrations of gases are in %-volume.

Location name		**Fumarole**
Temperature	**(°C)**	99
Coordinates	Northern	N11.22886
	Eastern	E41.85441
	Gas phase	
Ar	% Volume	0.74
CH_4	% Volume	1.59
H_2	% Volume	0
N_2	% Volume	38.86
O_2	% Volume	0.55
CO_2	% Volume	58.24
H_2S	% Volume	0.03
	Condensate phase	
B	mg/kg	0.03
Cl	mg/kg	0.13
Na	mg/kg	0.60
δD	‰ VSMOW	-33.55
$\delta^{18}O$	‰ VSMOW	-6.08
L gas / kg condensate		0.1534

In this area, only one sample was collected from a fumarole. Gas geothermometers were applied to the results of chemical analysis. Gas geothermometer temperature ranges (Table 5) are very large (20-250°C) and that is not a good sign. Because of the fact that there is only one sample, we cannot know if it is characteristic of the area and there is also no smell of H_2S indicating a high-temperature system. The sample is probably air contaminated; the significant values of O_2, N_2 and Ar (Table 4) allow the assumption that these gases were added to magmatic gas by atmospheric contamination because soil air contains oxygen, nitrogen and other trace atmospheric gases and these can be entrained in the steam discharge as it passes through the soil profile. These contaminations can also be added to a sample during the sampling process. Contamination of air, whatever the source is, changes the chemical composition of the sample and renders the gas geothermometers useless unless the contamination can be quantified. This fumarole cannot provide information about the area.

Table5: Calculated values for gas geothermometers temperatures (in °C) for Lake Abbe, Djibouti.

	T (°C)	Source	Range
CO_2	148	Arnórsson and Gunnlaugsson 1985	All waters
H_2S	141	Arnórsson and Gunnlaugsson 1985	All waters above 300°C
H_2S	20	Arnórsson and Gunnlaugsson 1985	All waters below200°C
CH_4/CO_2	250	Giggenbach (1991)	
CO_2	183	Arnórsson et al. 1998	> 100°C, basaltic rock
H_2S	48	Arnórsson et al. 1998	> 150°C, basaltic rock
CO_2/N_2	182	Arnórsson et al. 1998	if Ar and N_2 conc. in reservoir water are equal to those in air saturated water at 5°C
H_2S/Ar	87	Arnórsson et al. 1998	

3.5 Origin of the Water

3.5.1 Isotopes

The isotopic ratios correspond generally to small values and it is not easy to measure absolute isotopic ratios (Arnórsson, 2000). For this reason, isotopic concentrations are conveniently expressed in delta notation (δ) as parts per thousand. $\delta^{18}O$ and δD are related by the Global Meteoric Water Line (GMWL) developed by Craig (1961) and this GMWL is a result of climatic and geographic factors. There is also a Local Meteoric Water Line for Djibouti (LMWL; Fontes et al., 1980) which is derived from precipitation collected from local sites.

Stable $\delta^{18}O$ and δD isotopic analyses were used to determine the origin of thermal waters and the geothermal reservoir recharge area (Figure 6). The δD and δ18O values of meteoric waters at any locality are dependent upon latitude, altitude and distance from the ocean. In this study area, the oxygen and hydrogen isotopes are plotted and compared to the global meteoric water line (GMWL) and the local meteoric water line (LMWL). The equations of GMWL defined by Craig (1961) and LMWL defined by Fontes et al. (1980) are respectively: $\delta D = 8*\delta^{18}O + 10$ and $\delta D = 8*\delta^{18}O + 0$.

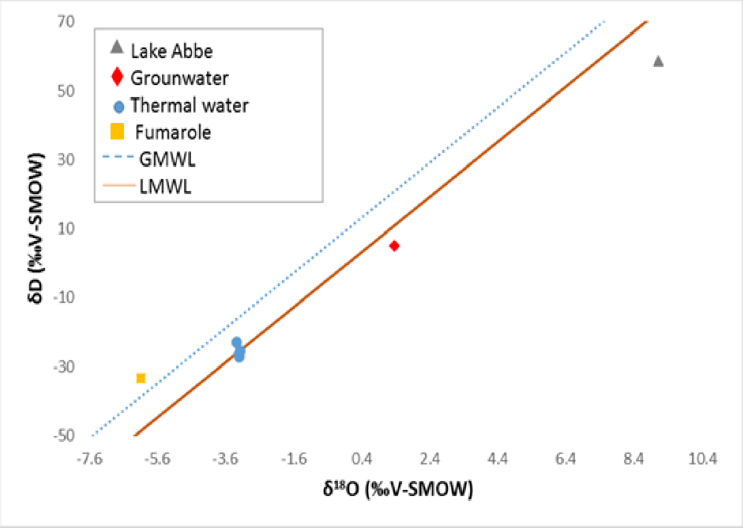

Figure6: Plot of δ18O-δD of the thermal waters and fumarole from Lake Abbe.

The thermal water is probably of local origin, plotting on the LMWL. The fumarole sample is more depleted in deuterium and oxygen-18, most likely due to boiling. It is probably from the same source as the thermal water, but it is very hard to say exactly because the fumarole is located very far away from the thermal water (approx. 12 km, see coordinates in Table 2). The cold groundwater comes from a different source than the thermal water because the difference in hydrogen isotopes is more than 30‰, indicating a different source. Lake Abbe water is highly evaporated, so it is normal to have higher values of 9.12‰ and 58.63‰ for $\delta^{18}O$ and δD respectively.

3.5.2 Cl/BRatio

The B and Cl contents of geothermal waters have been used to obtain information on the origin of these waters (White, 1957a, b; White et al., 1963; Truesdell, 1976) to evaluate mixing of hot and cold water in the upflow zones of geothermal systems and to assess other characteristics of such systems (Ellis, 1970; White, 1970; Fournier, 1977, 1979; Arnórsson, 1985; Janik et al., 1991; Truesdell, 1991).

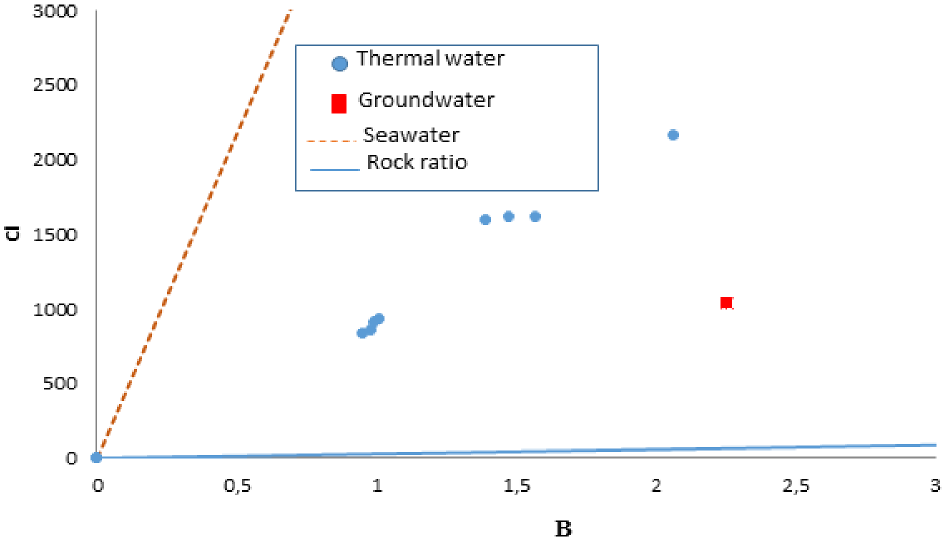

Figure 7: Distribution of Cl and B in thermal waters and groundwater in Lake Abbe area.

In the Figure 7, the rock ratio was assumed to be 30 because the study area is basaltic. The concentration of Cl in thermal water lies in the range of 835-2170 ppm and that of B in the range of 0.95-1.57 ppm. Their Cl/B ratio is on the range of 879-1151. This ratio is significantly higher than the Cl/B ratio in most analyzed basalts. The concentrations of B and Cl of thermal waters are somewhat higher than in groundwater and these areprobablydue to water rock interaction.

These thermal waters are from the same source which is suggested by the fact that they are all in the same line (Figure 7) while the concentration of B and Cl in groundwater are 2.25 ppm and 1040 ppm and it has the same Cl/B ratio as Lake Abbe. It is possible that the groundwater is related to Lake Abbe. The location of groundwater in Figure 7 indicates that it is probably comes from different source than thermal water. The concentration of B and Cl in Lake Abbe is very high (Table 2) and the Cl/B ratio is lower than thermal water. Due to the very different Cl/B ratios, despite the high Cl and B concentrations in Lake Abbe, it seems very likely that the thermal waters have a different origin than lake water.

3.5 Mineral Saturation

One of the most common production problems in geothermal fields is scaling deposition and corrosion. For that mineral equilibrium calculations are used to predict the presence of reactive minerals and to estimate mineral reactivity in a groundwater system. The saturation index was calculated for some minerals (calcite, quartz, chalcedony and anhydrite) using theWATCH chemical speciation model (Table 6). Available chemical analyses were entered into the WATCH program and the ion activity product (log Q) and solubility product (log K) of these minerals were computed, using the boiling springs model. The reference temperature used is measured temperature.

Table 6: Saturation index of the thermal waters from the study area.

	Calcite	Quartz	Anhydrite	Chalcedony	T(°C)
ABB1	0,568	0,398	-0,143	0,133	96,9
ABB2	0,579	0,384	-0,131	0,123	99,6
ABB3	0,718	0,315	-0,024	0,054	99,8
ABB4	0,742	0,284	-0,117	0,023	99,8
ABB5	0,738	0,317	-0,194	0,048	94,2
ABB6	0,788	0,318	-0,183	0,051	95,8
ABB7	0,807	0,289	-0,162	0,028	99,5
ABB12	0,493	0,404	-0,128	0,143	99,5
GW	0,507	0,583	-2,352	0,234	34

4. CONCLUSIONS

Analyses of geochemical data of thermal waters from hot springs and gas from fumaroles was carried out in order to estimate the subsurface reservoir temperatures and to investigate the origin of the waters. The thermal waters from the vicinity of Lake Abbe were found to be volcanic waters due to high concentrations of Cl and SO_4, and low concentration of CO_2. The Na-K-Mg ternary diagram indicates attainment of water-rock equilibrium. The reservoir temperatures were estimated using various solute geothermometers (silica, cation) which were found to be in the range of 107-160°C. This is in accordance with the Na-K-Mg ternary diagram which gives a similar range of temperature. Regarding the stable isotopic composition (oxygen and hydrogen), the thermal waters are meteoric water and have a different origin than the lake. The Cl/B ratios also suggest that these thermal waters are not derived from the lake. The saturation index of the thermal waters at the measured temperatures suggest that the thermal water in the study area is undersaturated with respect to anhydrite and supersaturated with respect to quartz, and calcite. However, these thermal waters are saturated with respect to chalcedony. The calcite deposits can be even observed, and the hypothesis is made that the formation of travertine was due to the precipitation of calcite.

The reservoir temperature was also calculated using gas geothermometers. The temperature range obtained is very large (20°-250°C) which indicates that the sample was probably air contaminated during sampling or was mixed with soil air that contains oxygen. This sampling was only from one fumarole, so it does not give information about the whole area.

Finally, geochemical studies and field observations suggest that the study area is a medium temperature geothermal system, which have to be confirmed by drilling. The other fumaroles found has to be sampled by a method other than the classic one.

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