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GEOCHEMICAL INTERPRETATION OF THERMAL WATER AND GAS SAMPLES FROM LAKE ABBE, DJIBOUTI

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ABSTRACT

The Lake Abbe geothermal area field is located in the south-western region of the Republic of Djibouti, on the border with Ethiopia. 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 analysed and 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 of 120-160°C. Hydrothermal data shows that the thermal waters have a high concentration of Cl which classifies them as volcanic waters and that these waters are equilibrated with the rock. The stable isotopic composition and Cl/B ratio were used to determine the origin of the water. The thermal waters are local meteoric waters from the same source and they are not mixed with Lake Abbe's water. The presence of the travertines shows that calcite deposition has occurred in the reservoir during geothermal production. The estimated reservoir temperatures suggest that the Lake Abbe geothermal area is a low-temperature geothermal system.

1. INTRODUCTION

The purpose of this report is to interpret the chemical data of thermal waters and gas from Lake Abbe, 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 sufficiently promising in terms of potential electricity generation utilising geothermal fluids.

The Lake Abbe zone is located in the south western region of the country, 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 in a large area of more than 100 km² in size with the surface temperatures of more than 90°C, and many spots with temperatures of 100-105°C. This observation suggests that in the Lake Abbe zone, an important thermal anomaly exist, 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 the ternary diagram, to estimate the reservoir temperature with geothermometers (quartz, cation and gas) and to determine the origin by interpreting the chloride and boron ratio and the stable isotopic composition (oxygen and deuterium).

2. METHODS

2.1 Field sampling

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 is recorded. An untreated sample is collected in an air-tight bottle for pH, CO₂, H₂S and conductivity measurements. If the subsurface temperature is assumed to be high, the sample is diluted with distilled and deionised water for analysis of SiO₂ to have an ideal concentration of 30 to 100 ppm. A filtered sample is collected for anions and a filtered and acidified sample is collected for cation analysis. The filter and the acid used have a 0.45 µm pore size membrane and suprapur acid HNO₃. To analyse SO₄, the sample is filtered and sulphide precipitated with zinc acetate; Zn(CH₃COO)₂. For the analyses of stable isotopes, the sample is filtered and collected to an airtight 60 mL glass bottle. The various sub-samples collected are described in detail in 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 ₂ S (<i>In situ</i>) | 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 | |
| Vapour | 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 ₂ S in NaOH | Gas chromatography, Titrimetry |

2.1.2 Sampling of fumaroles

The selection of fumaroles for sampling is not as straight forward as that of hot springs. It is generally best to sample small outlets which discharge steam at a considerable flow-rate 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 CO₂ and H₂S present in the steam dissolve quantitatively in the alkaline solution whereas the other gases remain in the head-space 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 CO₂ and H₂S in samples are analysed in a field laboratory the same day. The major chemical constituents in water samples are analysed in the geochemical laboratory using the analytical methods shown in Table 1.

3. GEOCHEMICAL METHODS IN GEOTHERMAL EXPLORATION: DIFFERENT GEOTHERMOMETERS

The application of chemical techniques has become an integral part of any geothermal exploration, especially in the early, pre-drilling stages (Giggenbach, 1991). Geochemical methods include sampling and analysis of water, gas and hydrothermal deposition. These methods are relatively inexpensive and can provide valuable information on the source of geothermal fluid and an estimation of temperature conditions in the geothermal reservoir using geothermometers. The soil gas measurements used around geothermal manifestations can allow estimation of the boundaries of the geothermal area and location of faults.

3.1 Geothermometry

The most commonly used “classic” solute geothermometers are the silica geothermometers (Fournier, 1977), Na/K geothermometers (White, 1965; Ellis, 1969; Fournier and Truesdell, 1973; Truesdell, 1975; Fournier, 1979), Na-K-Ca geothermometers (Fournier and Truesdell, 1973). The methods of chemical geothermometer allow, from the analysis of waters from the hot sources, to calculate the temperature at which they reached equilibrium with the host minerals. Various processes which can affect the chemical composition of deep hot waters, during their ascent and during their cooling since the geothermal reservoir towards the surface, the chemical geothermometers must be treated with caution according to the geologic environment where they are applied and according to the estimated ranges of temperature.

3.1.1 Silica geothermometers

The various silica phases (quartz, chalcedony and amorphous silica etc.) dissolve in water to reach equilibrium with aqueous H₄SiO₄.



The reaction of dissolution is independent of the pH and the ionic strength, thus the equilibrium state is essentially a function of temperature. Indeed, experimental results show that different solid phases of

silica (quartz, chalcedony and amorphous silica, etc.) have a solubility curve which varies with temperature (Fournier and Rowe, 1962).

The quasi-independence of the solubility of silica with regard to the ionic strength and the pH makes it possible to use the concentration of silica like geothermometer in the geothermic systems (Arnórsson, 1975; Truesdell, 1975). For higher temperature in the contents out of silica is generally controlled by quartz (Arnórsson, 1975). Between 120 and 180°C in fact the quartz or the chalcedony determines the solubility of silica; below 120°C only chalcedony.

It was reported that geothermal water boils in the process of rising towards the surface if the temperature of the reservoir exceeds 100°C (D'Amore and Arnórsson, 2000). This could cause inter alia an increase in the pH of thermal water because the dissolved acid gases (CO₂ and H₂S) are partitioned into the vapour phase during their ascent to the surface.

The silica geothermometers equations used to calculate subsurface temperatures are in Table 2.

TABLE 2: Temperature equations for silica geothermometers

| No. of equation | Geothermometer | Equation | Range (°C) | Reference |
|-----------------|----------------------|---|------------|----------------------------|
| 1 | Quartz-no steam loss | $T=1309 / (5.19 - \log S) - 273.15$ | 25-250 | Fournier (1977) |
| 2 | Quartz ^a | $T=1522 / (5.75 - \log S) - 273.15$ | 25-250 | Fournier (1977) |
| 3 | Quartz | $T=42.198 + 0.28831S - 3.6686 \times 10^{-4} S^2 + 3.1665 \times 10^{-7} S^3 + 77.034 \log S$ | 25-900 | Fournier and Potter (1982) |
| 4 | Quartz ^a | $T=-53.5 + 0.11236S - 0.5559 \times 10^{-4} S^2 + 0.1772 \times 10^{-7} S^3 + 88.390 \log S$ | | Fournier and Potter (1982) |
| 5 | Quartz | $T=-55.3 + 0.3659S - 5.3954 \times 10^{-4} S^2 + 5.5132 \times 10^{-7} S^3 + 74.360 \log S$ | 0-350 | Arnórsson et al (1998) |
| 6 | Quartz ^a | $T=-66.9 + 0.1378S - 4.9727 \times 10^{-5} S^2 + 1.0468 \times 10^{-8} S^3 + 87.841 \log S$ | 0-350 | Arnórsson (2000) |
| 7 | Chalcedony | $T=1032 / (4.69 - \log S) - 273.15$ | 0-250 | Fournier (1977) |
| 8 | Chalcedony | $T=1112 / (4.91 - \log S) - 273.15$ | | Arnórsson (2000) |

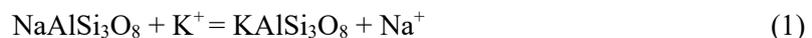
S represents silica concentration as SiO₂ in mg/kg.

^a Silica concentrations in water initially in equilibrium with quartz after adiabatic boiling to 100°C

3.1.2 Na/K geothermometers

It has been shown that the ratio between activity of sodium and potassium in a thermal solution is controlled by the chemical potential of these elements in silicates (Ellis and Mahon 1967).

The Na/K geothermometers are based on the equilibrium between a plagioclase and the K-feldspar. White (1965) and Ellis (1969; 1970) were the first to present the relationship between Na/K ratio and the temperature. They set related this with the equilibrium:



This relationship has, thereafter, been formulated in form of a thermometric relationship by Fournier and Truesdell (1973) and Fournier and Potter (1979) for temperatures above 120°C. Table 3 gives the Na/K geothermometers equations.

At lower temperatures, calcium usually compensates for significant fraction of cations and the Na/K geothermometers give to high temperature estimates for waters rich in calcium. Due of that, the Na-K-Ca geothermometer has been developed to estimate the temperature of those waters (Fournier and Truesdell, 1973).

TABLE 3: Temperature equations for Na/K geothermometers

| No. of equation | Geothermometer | Equation | Range (°C) | Reference |
|-----------------|----------------|--|------------|---------------------------|
| 9 | Na/K | $T = [856 / (0.857 + \log(\text{Na}/\text{K}))] - 273.15$ | 100-275 | (Truesdell, 1976) |
| 10 | Na/K | $T = [1217 / (1.483 + \log(\text{Na}/\text{K}))] - 273.15$ | | (Fournier, 1979) |
| 11 | Na/K | $T = [833 / (0.857 + \log(\text{Na}/\text{K}))] - 273.15$ | | (Tonani, 1980) |
| 12 | Na/K | $T = [933 / (0.857 + \log(\text{Na}/\text{K}))] - 273.15$ | 25-250 | (Arnórsson et al., 1983) |
| 13 | Na/K | $T = [1319 / (1.483 + \log(\text{Na}/\text{K}))] - 273.15$ | 250-350 | (Arnórsson et al., 1983) |
| 14 | Na/K | $T = [1178 / (1.470 + \log(\text{Na}/\text{K}))] - 273.15$ | | (Nieva and Nieva, 1987) |
| 15 | Na/K | $T = [1390 / (1.750 + \log(\text{Na}/\text{K}))] - 273.15$ | | (Giggenbach et al., 1988) |
| 16 | Na/K | $T = 733.6 - 770.551Y + 378.189Y^2 - 95.753Y^3 + 9.544Y^4$ | 0-350 | (Arnórsson et al., 1998) |

Na and K concentrations are given in mg/kg.

3.1.3 Na-K-Ca geothermometer

Fournier and Truesdell (1973) developed the Na-K-Ca geothermometers for application to waters with high concentrations of calcium. The cation geothermometers include the empirical Na-K-Ca geothermometer by Fournier (1981), which has been found to be consistent with measured well temperatures. This is an empirical geothermometer and theoretical constraints include equilibrium between Na-K feldspars plus conversion of calcium aluminosilicate minerals (e.g. Plagioclase) to calcite.

The main advantage of the Na-K-Ca geothermometer in comparison with the quartz geothermometer, and especially the Na/K geothermometer, is that it does not give high and misleading results for cold and slightly thermal, non-equilibrated waters.

The following considerations apply in application of this geothermometer:

$$T^{\circ}\text{C} = (1647 / (2.24 + \log(\text{Na}/\text{K}) + \beta * \log(\text{Ca}^{1/2}/\text{Na}))) - 273.15 \quad (2)$$

The methodology for the application of the Na-K-Ca geothermometer is as follows: Calculate the temperature using $\beta=4/3$ and cation concentrations expressed as mg/kg. If that calculated temperature is $< 100^{\circ}\text{C}$ or $[\log(\text{Ca}^{1/2}/\text{Na}) + 2.06]$ is negative, use $\beta=1/3$ to calculate the temperature (Arnórsson, 2000). Obviously, the Na-K-Ca geothermometer is applicable to a larger temperature range of thermal fluids than the Na/K geothermometer because the Na-K-Ca geothermometer appears to give excellent results for most waters above about 200°C , but erratic results are obtained for waters from reservoirs at less than 200°C . These erratic results appear to come from effects of high partial pressures of CO_2 and exchange reactions involving Na^+ , K^+ , or Ca^+ with additional ions (particularly Mg) (D'Amore, 1991). These are more or less the same limitations as for the Na-K geothermometer; it is also very good above 200°C (or 180°C) but often gives erratic results at lower temperatures. This geothermometer is affected by boiling and dilution.

3.1.4 Gas geothermometers

CO₂ in geothermal gas is mainly produced by volcanic activity while CH₄ is produced by two mechanisms: reduction of CO₂ but also the breakdown of organic matter by bacterial activity. H₂S is of magmatic origin but at very low concentrations and for H₂ some authors (D'Amore, 1991; Glover, 1970) propose an electrochemical origin of this gas (H⁺), produced by oxidation of sulphide. Chemical reactions in the steam due to oxidative contact with atmospheric gases, or the lowering of temperature may change the gas composition, hence it is necessary to sample the highest temperature fumaroles which guarantees the composition which is most likely to be representative of the source of the geothermal reservoir gas.

The gas geothermometers are often used to estimate deep temperatures in early exploration. Gas-gas or gas-mineral equilibrium is assumed to exist at the source (Óskarsson and Ármannsson, 2015), and they have the disadvantage of being more prone to errors than fluid geothermometers due to secondary processes. (Óskarsson, 2016). N₂ and Ar concentration are assumed to be source-controlled rather than equilibrium controlled, but CO₂, H₂S, H₂ and CH₄ are assumed to be controlled by equilibrium. The main gas geothermometers applied in this report can be seen in Table 4:

TABLE 4: Temperature equations for gas geothermometers

| Geothermometer | Temperature equations | Remarks |
|----------------------------------|--|---------------------------------|
| CO ₂ | $t^{\circ}\text{C} = 44.1 + 269.25Q - 76.88 Q^2 + 9.52 Q^3$ | All waters |
| H ₂ S | $t^{\circ}\text{C} = 246.7 + 44.8Q$ | All waters above 300°C |
| H ₂ S | $t^{\circ}\text{C} = 173.2 + 65.04Q$ | Arnórsson and Gunnlaugsson 1985 |
| CH ₄ /CO ₂ | $t^{\circ}\text{C} = [4625 / (10.4 + \log(\text{CH}_4/\text{CO}_2))] - 273.15$ | Giggenbach 1991 |
| CO ₂ | $t^{\circ}\text{C} = 4.724 Q^3 - 11.068 Q^2 + 72.012 Q + 121.8$ | Arnórsson et al. 1998 |
| H ₂ S | $t^{\circ}\text{C} = 4.811 Q^2 + 66.152 Q + 177.6$ | Arnórsson et al. 1998 |
| CO ₂ /N ₂ | $t^{\circ}\text{C} = 1.739 Q^3 + 7.599 Q^2 + 48.751 Q + 173.2$ | Arnórsson et al. 1998 |
| H ₂ S/Ar | $t^{\circ}\text{C} = 4.108 Q^2 + 42.265 Q + 137.6$ | Arnórsson et al. 1998 |

Q = log mmol/kg of gas

3.2 Classification and plots

Giggenbach (1991) proposed a SO₄-Cl-HCO₃ ternary diagram (Figure 1) for the initial classification of geothermal solutions to identify whether the geothermometers are applicable for the given water sample, as geothermometry assumes an equilibrium between fluid and rock at depth. A hot spring with significant chloride, moderate bicarbonate and minimal sulphate is consistent with outflow from a geothermal reservoir. It will be much more likely to provide reliable cation geothermometry than a spring that contains mainly bicarbonate or sulphate. When the fluid rises to the surface, the decrease of pressure can produce the evolution of a vapour phase which coexists with the liquid phase in the hydrothermal system. Then this vapour can either condense or dissolve in superficial ground water. To distinguish

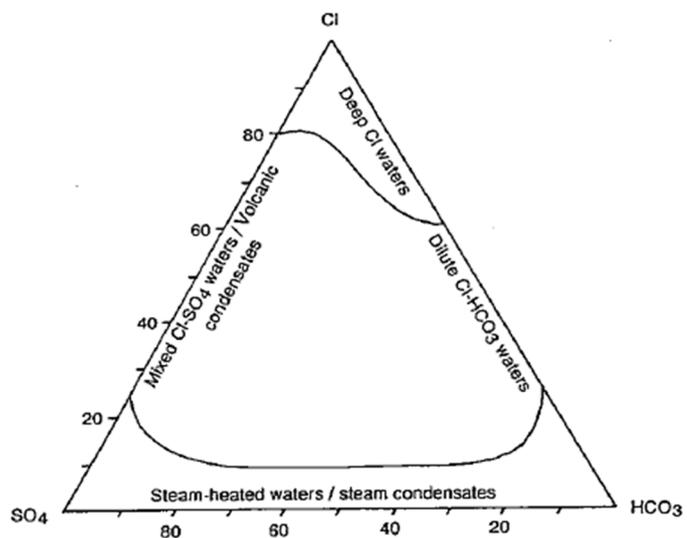


FIGURE 1: Ternary diagram Cl-SO₄-HCO₃

between those different types of fluids, a ternary diagram representing the proportion of chloride, sulphate and bicarbonate is used.

The interpretation of geothermal water chemistry is best carried out on the basis of an initial classification in terms of their major anions Cl, SO₄ and HCO₃. The position of a data point in such a triangular diagram (Giggenbach, 1991) is obtained by first calculating the sum S of the concentrations of all three constituents involved, which is in the present case:

$$S = C_{Cl} + C_{SO_4} + C_{HCO_3} \quad (4)$$

The next step consists the evaluation of %-Cl, %-SO₄ and %-HCO₃ according to the following equation:

$$\%Cl = 100C_{Cl}/S; \%SO_4 = 100C_{SO_4}/S; \%HCO_3 = 100C_{HCO_3}/S \quad (5)$$

4. APPLICATION OF THE CHEMICAL PROGRAM WATCH

The computer program WATCH (Arnórsson et al., 1982; Bjarnason, 2010) is used to calculate aqueous speciation in natural waters. Its primary area of application are geothermal fluids, but it is useful for non-thermal waters as well. The program reads chemical analyses of water, gas, and steam condensate samples collected at the surface and computes the chemical composition of downhole, aquifer or fluids at some suitably chosen reference temperature. WATCH is available for both Linux and Windows operating systems. A companion program, WAIN, is used to create input data files. The concentrations of the species considered in the program are expressed in terms of the component concentrations by mass balance equations. The chemical equilibria between the species are also expressed as mass action equations. The program contains provisions for 69 different aqueous species which are treated separately.

The output from the program lists the component and species concentrations in the deep fluid at the reference temperature as well as the activity coefficients. Finally, the ion activity products log Q and solubility products log K of selected minerals are computed and printed. From these, it is straightforward to compute the corresponding saturation indices log Q/K.

In this study, the WATCH program is used to estimate and evaluate the state of saturation of common scale forming minerals. This saturation index is useful in the study of scaling.

5. LAKE ABBE GEOTHERMAL FIELD, DJIBOUTI

5.1 Geology of the country

The Republic of Djibouti is located within the Afar depression, which is a big crustal zone resulting from the separation of the Arabian and African plates. This zone establishes the connection between the current oceanic ridge in the Red Sea and the Gulf of Aden system, which evolved into laterally intra-continental rifts. The geology of the country is affected by the junction of the Aden gulf, the Red Sea oceanic ridge, and also by the East African rifting system which constitute the triple junction system (McKenzie et al., 1970) (Figure 2). Almost all of the Afar depression is covered by stratoid basalts, which are partially hidden and were created in the early stages of rifting (Barbéri et Varet, 1975).

The republic of Djibouti has been the place of a major tectonic activity since the Oligo-Miocene period until today. All stages of rifting have occurred there which were followed by the formation of the Afar depression. This is why all the different geological formations can be found in the Republic of Djibouti.

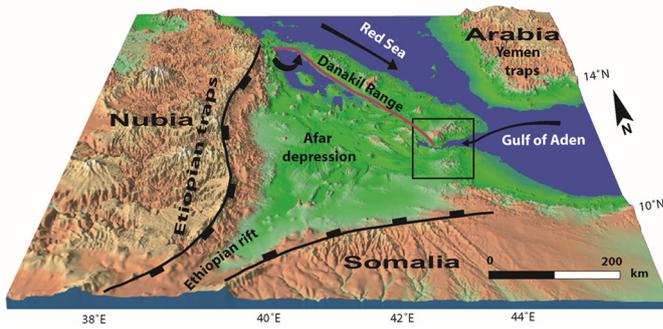


FIGURE 2: The rifting system and Afar depression

Almost all the rocks in the country are of basaltic composition (Figure 3) and Quaternary sediments are found in the north of the country. In Figure 3, surface manifestations are shown by dots which are located mainly on the rift stream bed (SW-NE trend). About thirteen geothermal provinces have been identified in the country according to the location of surface manifestations. The study area is one of them: Lake Abbe, the red circle in the Figure 3.

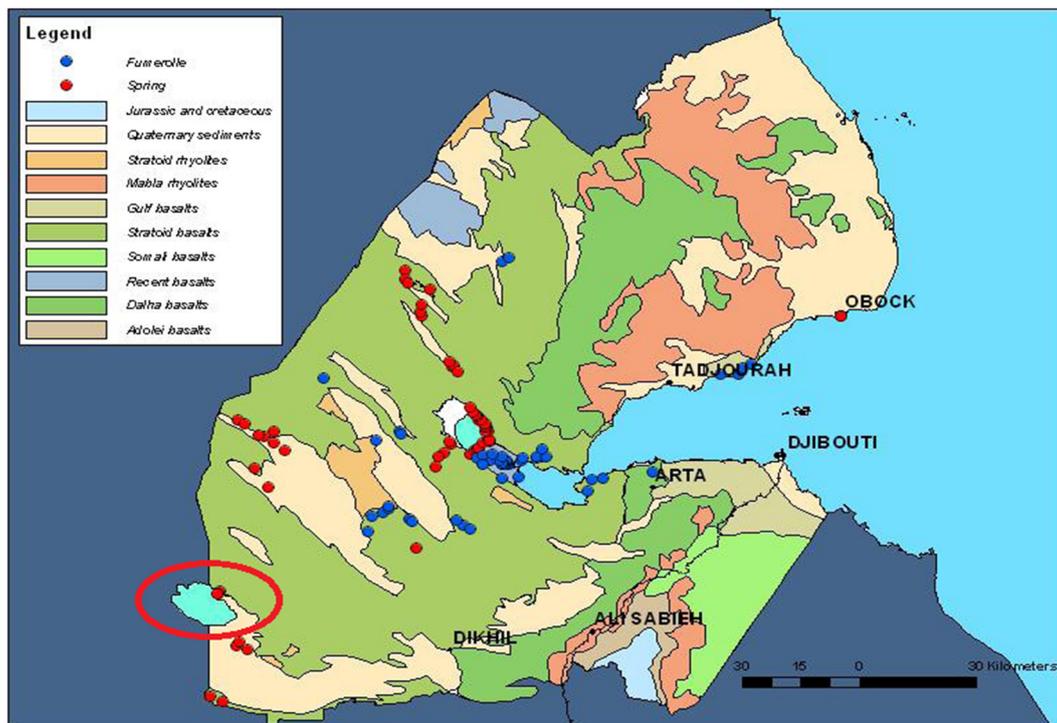


FIGURE 3: Geological Maps of Djibouti (CERD). The red circle shows Lake Abbe

5.2 Regional geology: Lake Abbe

The Lake Abbe site is located in the south-western region of the Republic of Djibouti near the Ethiopian border. It is the western end of the Goba’ad plain and the eastern end of the downstream valley of the Awash River from the Ethiopian plateau. Its surface covers an area of about 150 km² and trends to 240 m of altitude. The Lake Abbe is the remainder of an old lake from 6000 years ago surrounded by volcanoes and is marked out by its calcium chimney edified on fractures related to the collapse of the region. The travertines were formed under water. The highest is about 60 m (Figure 4). These travertines are formed inside the lake where hot springs with high calcium concentration rise up through fractures and it mixes with the cold lake water. This causes precipitation and deposition of calcite throughout the orifice of the outflow. Thus, the travertines were formed in some thousands of years (Pantecost and Viles, 1994). The most characteristic feature of the Lake Abbe region is the presence of a linear chain of travertine chimneys and the temperature of resurgence of the hot springs being generally higher than 90°C. The area is still in formation due to the ongoing movement of the divergent plate boundary.

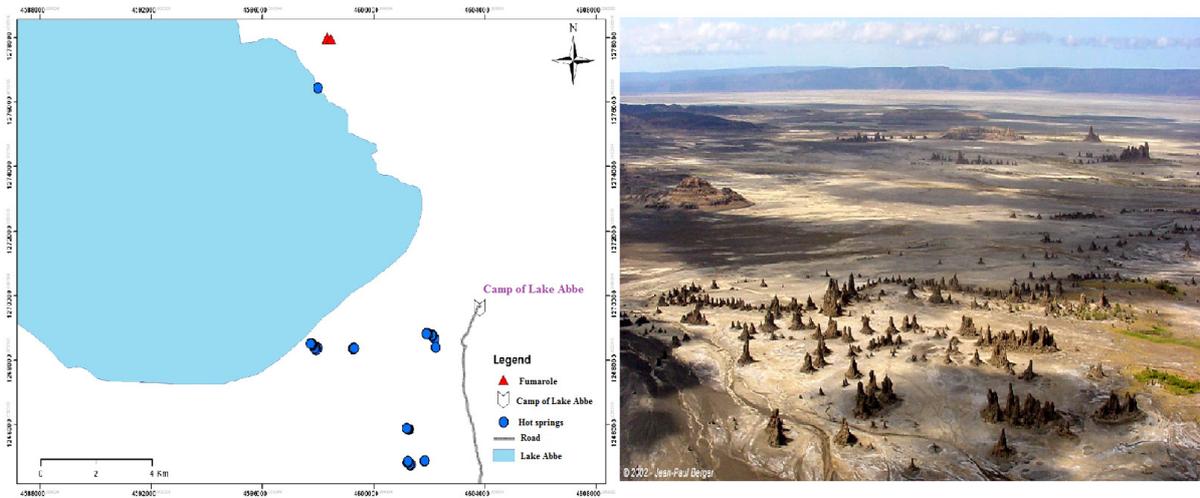


FIGURE 4: Location map of geothermal manifestations (left). Travertine chimneys (right)

Stratoid basalt (3.5-1 Ma) and recent cinder cones dominate the site, which lies at the eastern coast of Lake Abbe, the Goba'ad basin and the north-eastern horst (240 to 560 m high). Several rhyolitic intrusions-pyroclastic are distributed along the south-eastern margin. Lacustrine, calcareous and salty sediments fill every small polygonal depressions and the basin (Sabkha) up to salty Lake Abbe. Major WNW fracture systems are parallel to graben and horst structures, while minor transversal NNE trend fractures are also recognized. Recent cinder cone distributions seem to be controlled by intersection positioning of the two fracture systems. Scattered acidic alteration spots or small mounds (sinter cones) are common in the recent pyroclastic cone foothill and rhyolite related alteration is scarce at this site.

6. RESULTS AND DISCUSSIONS

In this study, samples from eight hot springs, one cold groundwater spring and one fumarole were collected (Fig 4) and analysed. The major, minor and trace elements of these waters are reported in Appendix II. The temperature of the geothermal water samples of Lake Abbe ranged from 94.2 to 99.8°C. The conductivity of these waters ranges between 3140-7210 $\mu\text{S}/\text{cm}/^\circ\text{C}$.

6.1 Cl-SO₄-HCO₃ ternary 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-SO₄-HCO₃ in Figure 5, 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, 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.

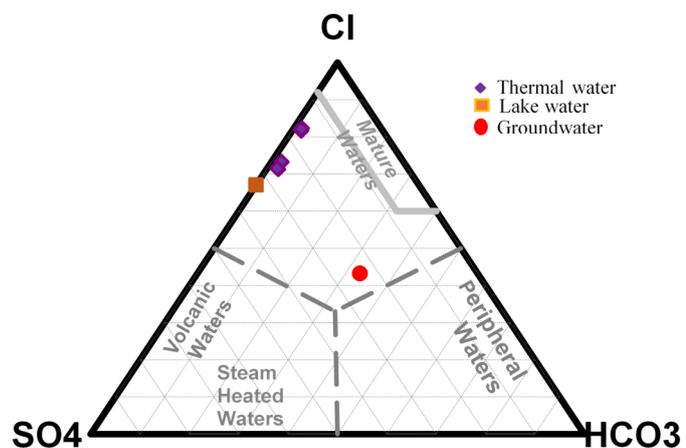


FIGURE 5: Cl-SO₄-HCO₃ Ternary diagram

6.2 Na-K-Mg ternary diagram

The ternary diagram of Na-K-Mg shown in Figure 6 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. Fournier (1990) states that the diagram is most useful for determining which waters are most suitable for geothermometry. 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.

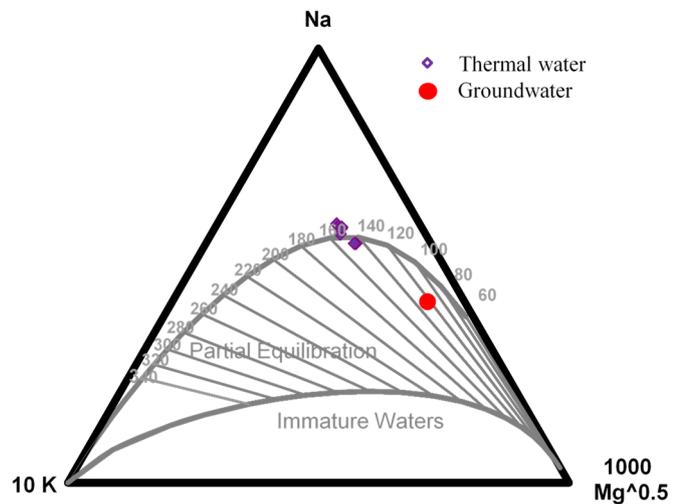


FIGURE 6: Na-K-Mg ternary diagram for Lake Abbe water samples

Figure 6 shows that the samples from thermal water are fully equilibrated or close to equilibration, whereas the groundwater sample is only partly equilibrated. It is normal that this water is not at equilibrium because at low temperatures the reactions between the water and the rock are very slow. The thermal water appears to be well equilibrated at temperatures of 140-160°C according to the Na-K-Mg ternary diagram.

6.3 Geothermometers of Lake Abbe

6.3.1 Silica and cation geothermometers

In this paper, nine geothermometers equations were used (Table 5): three for quartz, three for Na-K, two for chalcedony, and 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 (Table 2). For the Na/K geothermometer also three equations were chosen: equations 12, 14 and 16 (Table 3). 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.

Figure 7 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 Appendix II 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.

TABLE 5: Calculated values for 9 equations for solute geothermometers temperatures (in °C) for Lake Abbe, Djibouti

| Name | Quartz | | | Na-K | | | Chalcedony | | Na-K-Ca |
|---------|--------------------|--------------------|--------------------|-----------------------|-----------------------|-----------------------|--------------------|--------------------|----------------------|
| | T _{qz, 2} | T _{qz, 4} | T _{qz, 6} | T _{Na-K, 12} | T _{Na-K, 14} | T _{Na-K, 16} | T _{ch, 7} | T _{ch, 8} | T _{Na-K-Ca} |
| 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 |

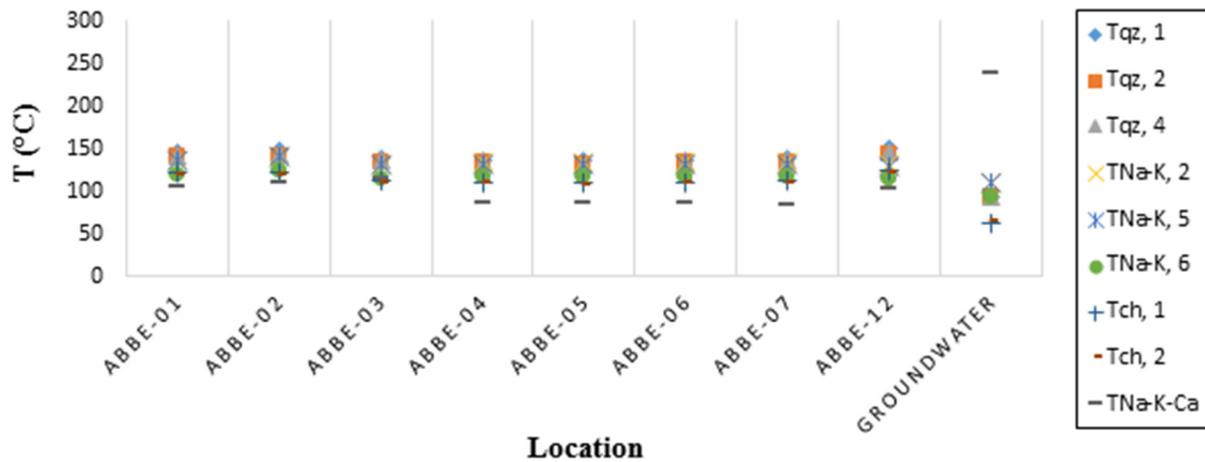


FIGURE 7: Calculated temperature results obtained with silica, Na-K and Na-K-Ca geothermometers

6.3.2 Gas geothermometers

The following gases are invariably present in geothermal discharges from both natural features and wells: CO₂, H₂S, N₂, H₂, CH₄, NH₃. So it is important to know the behaviour of these geothermal gases (Appendix I).

In this area, only one sample was collected from a fumarole. Gas geothermometers (Table 4) were applied to the results of chemical analysis. Gas geothermometer temperature ranges (Table 6) 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 H₂S indicating a high-temperature system. The sample is probably air contaminated, the significant values of O₂, N₂ and Ar (Appendix I) 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.

TABLE 6: Calculated values for gas geothermometers temperatures (in °C) for Lake Abbe, Djibouti

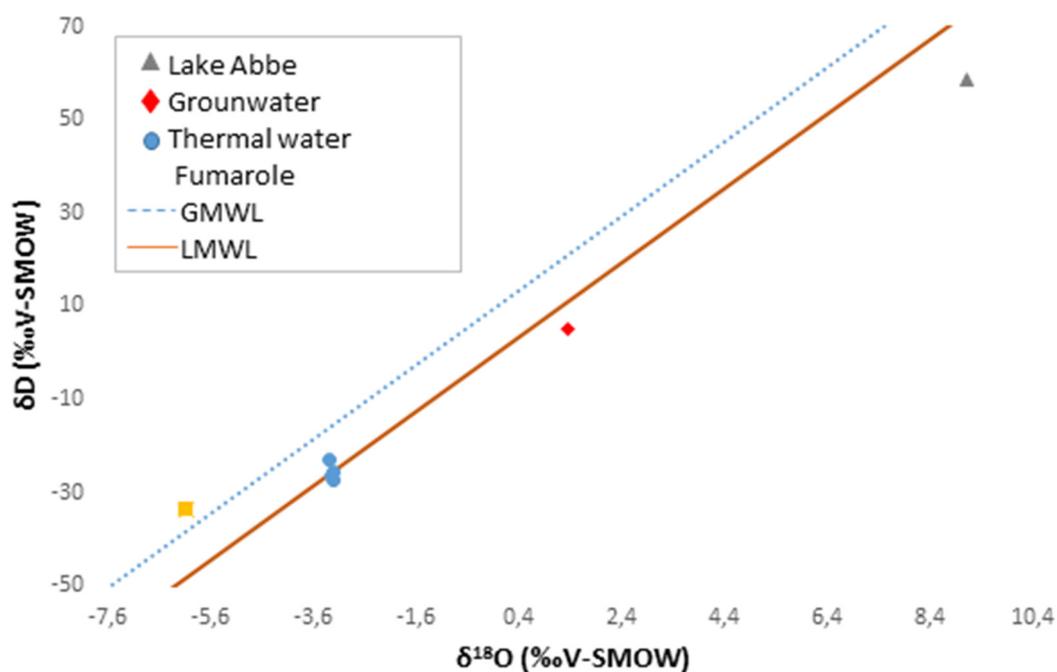
| | T | Source | Range |
|----------------------------------|-----|---------------------------------|--|
| CO ₂ | 148 | Arnórsson and Gunnlaugsson 1985 | All waters |
| H ₂ S | 141 | Arnórsson and Gunnlaugsson 1985 | All waters above 300°C |
| H ₂ S | 20 | Arnórsson and Gunnlaugsson 1985 | All waters below 200°C |
| CH ₄ /CO ₂ | 250 | Giggenbach (1991) | |
| CO ₂ | 183 | Arnórsson et al. 1998 | > 100°C, basaltic rock |
| H ₂ S | 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 ₂ S/Ar | 87 | Arnórsson et al. 1998 | |

6.4 Origin of the water

6.4.1 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. $\delta^{18}\text{O}$ and δD are related by the Global Meteoric Line water (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 $\delta^{18}\text{O}$ and δD isotopic analyses were used to determine the origin of thermal waters and the geothermal reservoir recharge area (Figure 8). The δD and $\delta^{18}\text{O}$ values of meteoric waters at any locality is 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 line (GMWL) and local meteoric line (LMWL). The equations of GMWL defined by Craig (1961) and LMWL defined by Fontes et al. (1980) are respectively: $\delta\text{D} = 8 \cdot \delta^{18}\text{O} + 10$ and $\delta\text{D} = 8 \cdot \delta^{18}\text{O} + 0$.

FIGURE 8: Plot of $\delta^{18}\text{O}$ - 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 waters 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 Appendix II). The cold groundwater comes from different source than thermal water because the difference in hydrogen isotopes is more than 30‰ indicating a different source. Lake Abbe water is much evaporated so it is normal to have higher values of 9.12‰ and 58.63‰ for $\delta^{18}\text{O}$ and δD respectively.

6.4.2 Ratio Cl/B

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).

In the Figure 9, the rock ratio was assumed 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 analysed basalts. The concentrations of B and Cl of thermal waters are somewhat higher than in groundwater and these are due probably to water rock interaction. These thermal waters are from the same source which is shown by the fact that they are all in the same line (Figure 9) 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 9 indicates that it is probably comes from different source than thermal water. The concentration of B and Cl in Lake Abbe is very high (Appendix II) 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.

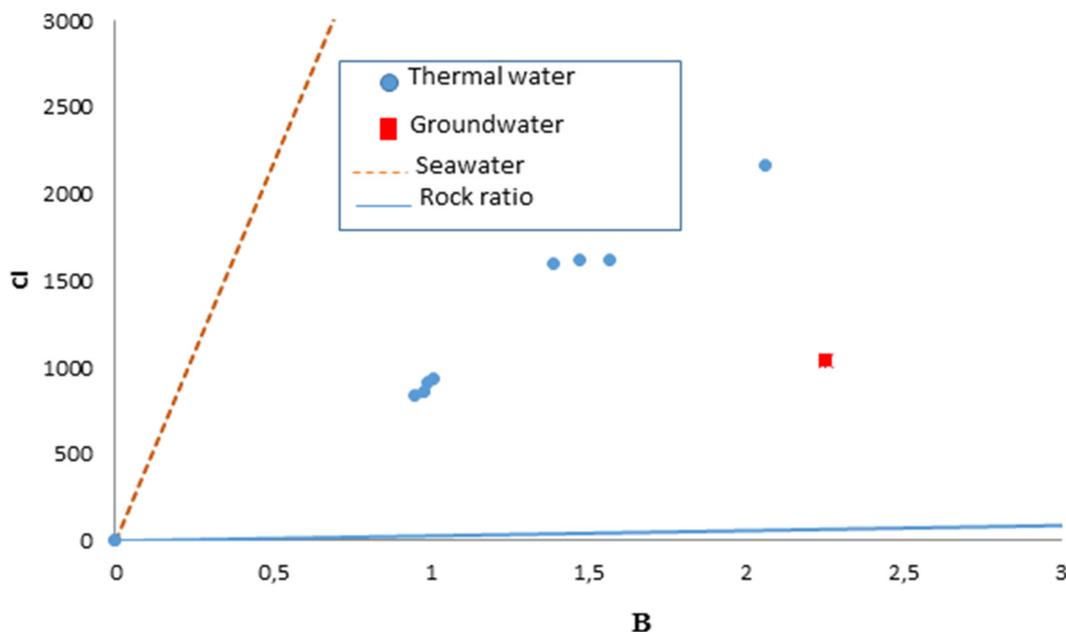


FIGURE 9: Distribution of Cl and B in thermal waters and groundwater in Lake Abbe area

6.5 Mineral saturation index

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 a chemical speciation model, the WATCH program (Table 7). 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 7: Saturation index of the thermal waters from the study area

| | Calcite | Quartz | Anhydrite | Chalcedony | T |
|-------|---------|--------|-----------|------------|------|
| 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 |

All thermal waters of the study area are undersaturated with respect to anhydrite (CaSO_4) at sampling conditions but might be saturated at reservoir temperatures. The silica minerals (quartz, chalcedony) were found to be oversaturated and near equilibrium state. It is normal for the silica minerals to be in equilibrium, their reactions are pretty fast (at least for chalcedony at this temperature) and if they were not in equilibrium we could not use the silica geothermometers. Silica minerals are most likely to precipitate as scales from the geothermal waters during geothermal production. Regarding calcite scaling, all thermal waters are oversaturated and the saturation index (SI) is between 0.493 and 0.807. If the SI is higher than 0.38, the potential for calcite scaling exists (Bai, 1991). This is the case of the study area and it is shown by the presence of calcite travertines in Lake Abbe area.

7. 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 120-160°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. 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, chalcedony and calcite. The calcite deposits can be even observed and the hypothesis is made that the formation of travertines was due to the precipitation of calcite.

The reservoir temperature was calculated also 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 low temperature geothermal system, which has to be confirmed by drilling. The others fumaroles found have to be sampled by other method than the classic one.

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APPENDIX I: Chemical composition of fumarole in Lake Abbe geothermal area

| Location name | | Fumarole |
|------------------------------|------------------|-----------|
| Temperature | (°C) | 99 |
| Coordinates | Northern | N11.22886 |
| | Eastern | E41.85441 |
| Gas phase | | |
| Ar | % Volume | 1.76 |
| CH ₄ | % Volume | 3.81 |
| H ₂ | % Volume | 0 |
| N ₂ | % Volume | 93.11 |
| O ₂ | % Volume | 1.32 |
| CO ₂ | mg/kg condensate | 380 |
| H ₂ S | mg/kg condensate | 0.15 |
| Condensate phase | | |
| B | mg/kg | 0.03 |
| Cl | mg/kg | 0.13 |
| Na | mg/kg | 0.60 |
| δD | ‰ VSMOW | -33.55 |
| δ ¹⁸ O | ‰ VSMOW | -6.08 |
| L gas / kg condensate | | 0.1534 |

APPENDIX II: Chemical data of springs in Lake Abbe geothermal area

| location name | Abbe-01 | Abbe-02 | Abbe-03 | Abbe-04 | Abbe-05 | Abbe-06 | Abbe-07 | Abbe-12 | Groundwater | Lake Abbe |
|-------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|-----------|
| Coordinates | N11.14745 E41.88131 | N11.14851 E41.87919 | N11.14631 E41.84077 | N11.12268 E41.87017 | N11.14502 E41.89090 | N11.11385 E41.87503 | N11.11298 E41.86997 | N11.14483 E41.88167 | N11.12764 E41.89419 | - |
| Temperature (°C) | 96.9 | 99.6 | 99.8 | 99.8 | 94.2 | 95.8 | 99.5 | 99.5 | 34 | - |
| Conductivity | 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 | 1.47 | 1.39 | 2.06 | 1.01 | 0.99 | 0.98 | 0.95 | 1.57 | 2.25 | 100 |
| Br | 7.21 | 7.16 | 9.62 | 4.51 | 4.38 | 4.26 | 4.03 | 7.38 | 5.26 | 209 |
| Ca | 225 | 217 | 262 | 177 | 173 | 161 | 157 | 223 | 3.87 | - |
| Cl | 1620 | 1600 | 2170 | 935 | 912 | 863 | 835 | 1620 | 1040 | 39200 |
| CO ₂ | 20.8 | 25.1 | 29.2 | 18 | 16.5 | 20.5 | 17.6 | 22.4 | 572 | - |
| F | 0.94 | 1.15 | 0.97 | 0.85 | 0.82 | 0.83 | 0.84 | 1.21 | 5.26 | 138 |
| Fe | 0.03 | 0.03 | 0.04 | 0.03 | 0.02 | 0.03 | 0.02 | 0.04 | 0.05 | - |
| H ₂ S | 0.02 | 0.01 | 0.03 | 0.03 | 0.03 | 0.02 | 0.04 | 0.03 | 0.04 | - |
| K | 28.3 | 30.5 | 35.4 | 15.7 | 15.5 | 15 | 14.7 | 25.8 | 22.8 | - |
| Mg | 0.18 | 0.38 | 0.51 | 0.06 | 0.05 | 0.05 | 0.08 | 0.17 | 2.45 | - |
| Na | 950 | 950 | 1310 | 567 | 558 | 537 | 527 | 960 | 1280 | - |
| SiO ₂ | 118 | 120 | 104 | 100 | 97 | 100 | 103 | 125 | 40.5 | - |
| SO ₄ | 328 | 325 | 426 | 319 | 308 | 319 | 308 | 322 | 573 | 19300 |
| UE | 3570 | 3630 | 4660 | 2370 | 2320 | 2200 | 2170 | 3550 | 3470 | - |
| HCO ₃ | 28.84 | 34.80 | 40.48 | 24.95 | 22.88 | 28.42 | 24.40 | 31.05 | 793.00 | - |
| δD | - | -25.55 | -23.1 | -27.29 | - | - | -26.62 | - | 4.94 | 58.63 |
| δ ¹⁸ O | - | -3.17 | -3.26 | -3.2 | - | - | -3.22 | - | 1.38 | 9.12 |