GEOCHEMICAL INTERPRETATION OF THERMAL WATER AND BOREHOLE WATER FROM THE ASAL-GHOUBBET REGION, DJIBOUTI

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ABSTRACT

The Asal area, Djibouti, is characterized by volcanic activity with extensive faulting, hot springs and fumarole manifestations on the surface. Geologically, this area is dominated by volcanic rocks like basalts. Twenty-eight samples were collected from springs and Asal wells in 1990 from the Asal-Ghoubbet area. The purpose of this project is to interpret the chemical data obtained from these samples using the Cl-SO_4-HCO_3 and Na-K-Mg ternary diagrams for classification of the water and to estimate the temperature and origin of the reservoir fluids from the results of chemical analysis. Apparently, chalcedony controls the silica solubility and the results of original cation geothermometer calculations suggest a much higher temperature for the Na-K-Ca geothermometer than the Na/K geothermometer, for the spring waters. The high Na-K-Ca temperatures are due to the influence of cold groundwater and after the application of a magnesium correction, values much closer to those of the other geothermometers are obtained. Quartz controls the silica solubility in the fluids of the Asal wells, and the quartz geothermometer yields temperatures close to measured temperatures as do the cation geothermometers (Na-K and Na-K-Ca). The Cl/B concentration ratios suggest that the spring water composition is influenced by water-rock interaction, but that of the borehole water suggests evaporated seawater with a relatively low boron concentration. Thus, the results of this study suggest that the spring waters are mostly relatively low temperature waters whose origin is in seawater and whose composition has been modified by evaporation and water-rock interaction. The Asal well water is predominantly evaporated seawater from a reservoir with temperatures of 220-260°C.

1. INTRODUCTION

The Republic of Djibouti (surface area 23,000 km^2) is one of several African countries located on the East African rift system, whose geology is also a result of two other ridges in the Red Sea and the Gulf of Aden**.**
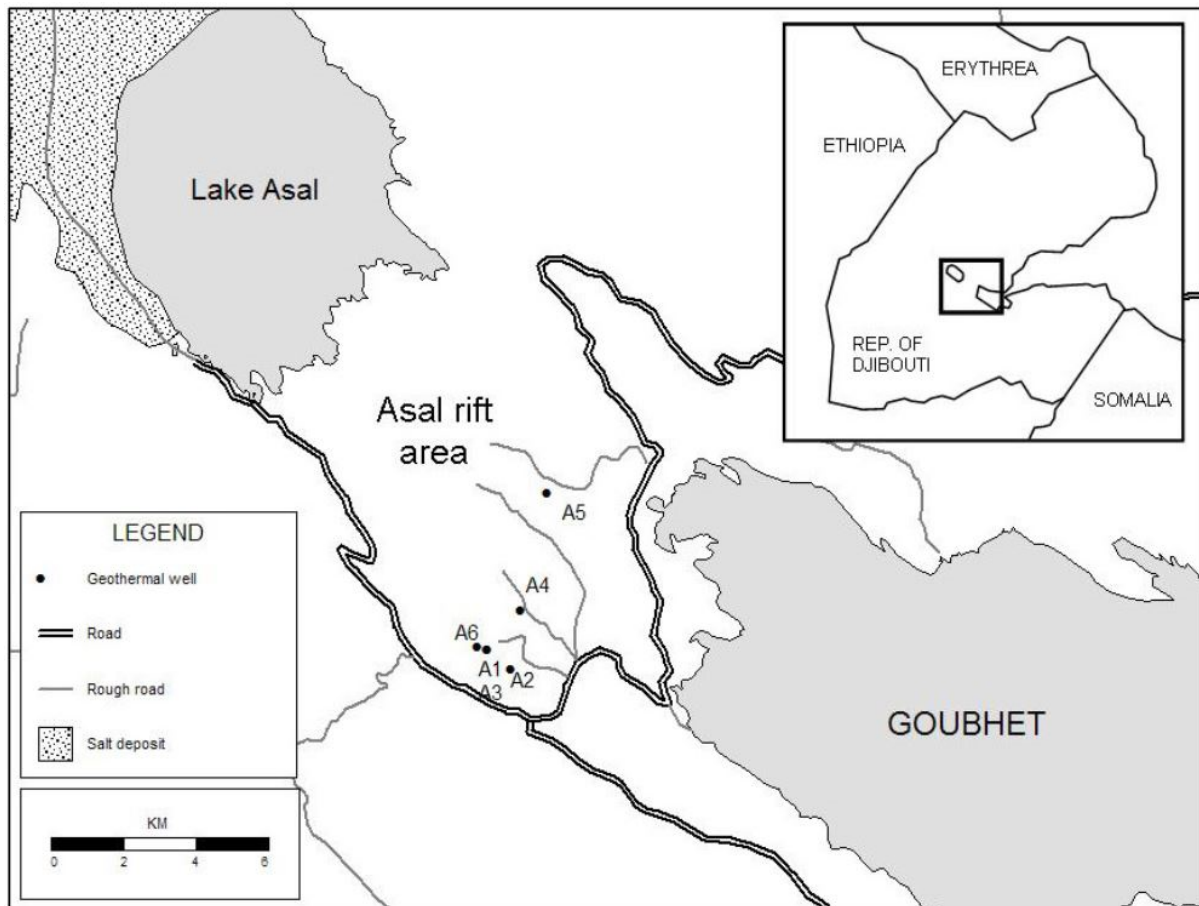
FIGURE 1: Asal geothermal field (from Elmi Houssein, 2005)

The Asal area (Figure 1) is located in the Afar depression at the bottom of the Gulf of Tadjourah. The first geothermal investigations in this area were undertaken in 1970 and included geological and geochemical studies, as well as geophysical exploration (Elmi Houssein and Axelsson., 2010; BRGM, 1973). The existence of a shallow crust-melting zone, important seismic activity, the presence of fumaroles and hot springs make it possible to classify this region as a zone with a high geothermal potential (Sanjuan et al., 1990, Barberi et al., 1980).

Most importantly, a high-temperature geothermal system was established in the Asal field where six deep wells have been drilled (Figure 1) (BRGM, 1973). Wells Asal 1 and 2 were drilled in 1975 by BRGM (BRGM 1975a, b, 1980, Barbut et al., 1982 and wells Asal 3 to Asal 6 in 1987/1988 by Intairdrill Ltd. supervised by Aquater (Aquater 1987, 1988, 1989 a, b). The salinity of the water of this region is high and the maximum salinity of the water from Lake Asal is 9 to 10 times greater than that of seawater.

The purpose of this study is to interpret the chemical properties of surface thermal water from the Asal area and the water from wells Asal 1, 3 and 4 using ternary diagrams to determine the water type and the maturity of the geothermal water, and also to estimate the reservoir temperature using chalcedony, quartz, Na/K and Na/K/Ca geothermometers.

2. BACKGROUND OF THE ASAL GEOTHERMAL FIELD

The Republic of Djibouti is covered by volcanic rocks and thermal manifestations are widespread. The Asal Rift is the most active structure in the Afar depression and is characterized by a volcanic series mainly consisting of basalts.

2.1 General geological setting

Asal (alternative spelling: Assal), the most important geothermal area in Djibouti, is in an active rift zone (Figure 1) on the isthmus between Lake Asal, which is 160 m below the sea water level and the lowest point in Africa, and Ghoubet al Kharab at a distance of 120 km from Djibouti town. The Asal region has several surface manifestations, such as hot springs and fumaroles. Warm springs are abundant along the east side of Lake Asal with temperatures varying from 30°C to 90°C and the temperature of the borehole thermal water ranges from 260 to 280°C and even higher (Sanjuan et al. 1990).

This region is characterized by extensive faulting and volcanic activity (Figure 2) with the latest eruption taking place in 1978 (Árnason and Flóvenz, 1995). The external rift is manifested by large normal faults and the inner rift is characterized by vertical faults as well as by intense fracturing and recent lava flows where the Korilii (AS1) and Manda areas (AS2, AS3, AS4, AS5, AS9, and AS10) with thermal water springs are located. A major fault intersects Lake Asal where the Eadkorar (AS 6 and AS 7) and Kalou Wadi (K1, K2, K4, K5 and K6) groups of hot springs are located (Figure 3).
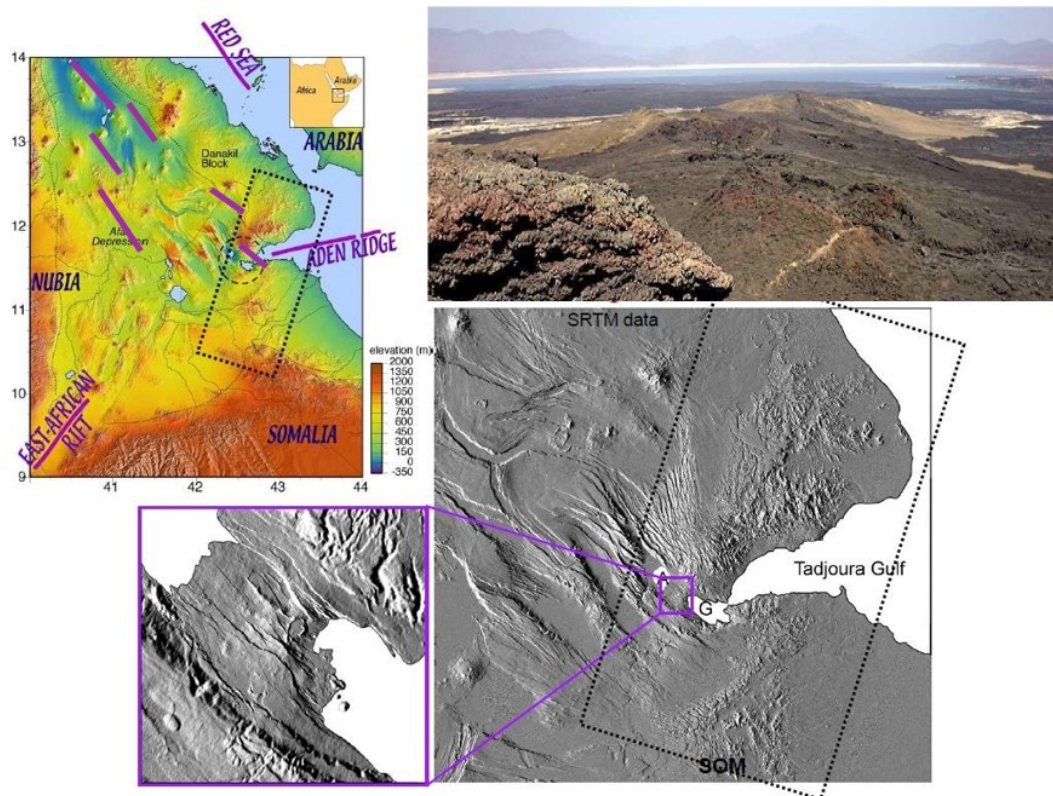

FIGURE 2: Location of the Asal geothermal site at the first emerged rift segment in SE Afar,
where the axial volcanic ranges (in violet) meet the Aden ridge through the
Gulf of Tadjourah and the Ghoubbet Bay (G) (Varet, 2014)

The main geological units in the Asal rift area are of a basaltic origin (Figure 2). The results of analysis of drill cuttings from wells drilled in the rift show that the stratigraphic column in the area is composed of, from top to bottom:

- The Asal series: basalts and hyaloclastites less than 1 Ma old,
- The Afar stratoid series: basalts with some rhyolites 1-4 Ma old, where AS6, AS7, AS8, AS11 and AS12 are located.
- The Dala Basalt: basaltic lava flows with some intercalations of rhyolites and trachyte 4-9 Ma old which is the component of the reservoir of Asal 1, Asal 3 and also Asal 4 (Elmi Houssein and Axelson, 2010).
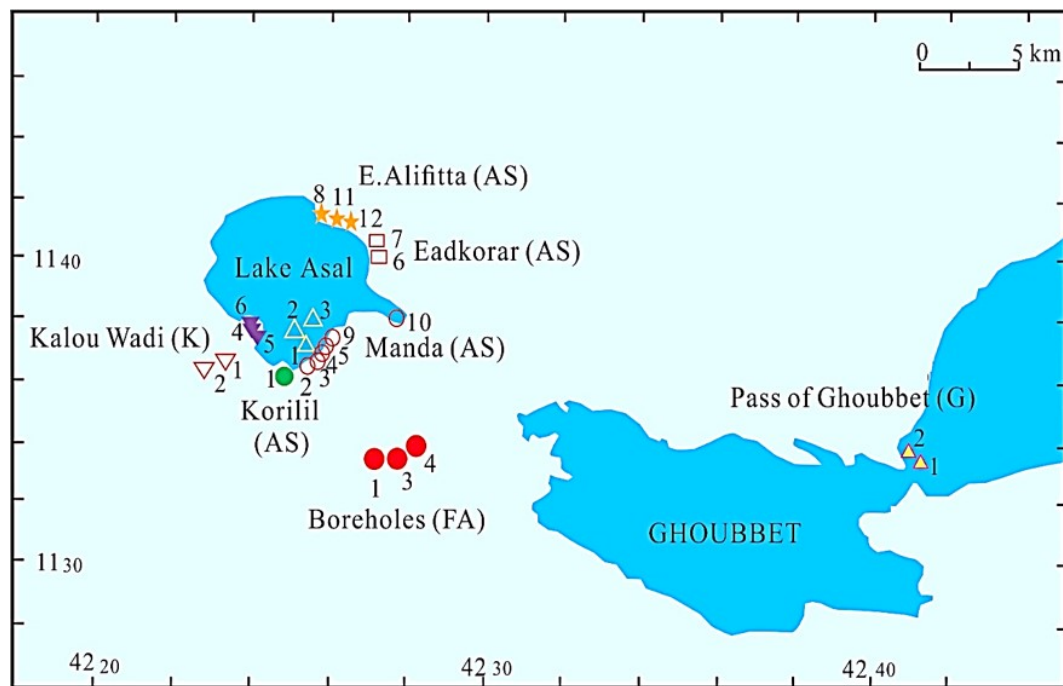
FIGURE 3: Map of the Asal-Ghoubbet area

The thermal water on the edge of the Ghoubbet (G2) is located in the basaltic series of the Gulf (1-4 Ma). Finally, Lake Asal is located in the pit that resulted from the collapse of the stratoid basalt series.

2.2 Wells drilled in the Asal area

In the Asal area, six wells have been drilled (Table 1). The first two wells were drilled in 1975 by BRGM. The depth of Asal 1 was 1554 m and the second well Asal 2 (located 800 m southwest of Asal 1) 1147 m. The other wells (3, 4, and 5) were drilled by Intairdrill Ltd. and supervised by Aquater in 1987-1988. Asal 1, 3 (1361 m), and 6 (1761 m) are located in the southern zone of the Asal rift inside the half circle of hyaloclastites known as Gale le Koma (Souleiman, 2010; Elmi Houssein, 2005) where Asal 6 was drilled by ISERST (Institut supérieur d'études et de recherches scientifiques et techniques). These wells have produced extremely saline fluids (130 g/l), about 3.5 times the salinity of seawater, from between 1000 and 1300 m depth. These wells also share the same reservoir with an aquifer temperature between 260 and 280°C. Wells Asal 3 and 6 are the only two wells which are currently productive. Asal 4 and 5 are located towards the centre part of the rift. Their final depths reached 2013 and 2105 m respectively, and they encountered a superficial, underground sea water flow at depths between 250 m and 280 m. Despite these greater depths, no deep reservoir was encountered although the bottom-hole temperatures reached 345°C and 359°C respectively. The characteristics of the Asal wells, such as the depth of the wells, the maximum temperature, the salinity etc. are summarized in Table 1.

From October 1989 to April 1990, the Virkir-Orkint Consulting Group Ltd. (Virkir-Orkint, 1990) made a study of the wells in the Asal area. This study was carried out to assess the effect of scaling/corrosion and to determine the optimum level of production for each well with time.

With a pH of 4 to 5 and a chemical fluid composition that is basically sodium and calcium chloride, the fluid from the Asal wells is supersaturated with respect to several minerals such as silica, iron silicate and several metal sulphides. The concentration of silica was equivalent to that expected from a reservoir temperature of 260°C, which is the reservoir temperature of Asal 1 and 3.

TABLE 1: Characteristics of Asal wells (Souleiman, 2010)

Drilled wells	Beginning of drilling	End of drilling	Final depth (m)	Temperature maximum (°C)	Total flow (ton/h)	Salinity (g/l)
Asal 1	9.3.1975	6.6.1975	1146	260	130 (WHP = 6 bar)	120
Asal 2	4.7.1975	15.9.1975	1554	235	-	-
Asal 3	11.6.1987	11.8.1987	1316	260	350 (WHP = 12.5 bar)	130
Asal 4	15.9.1987	20.12.1987	2013	345	-	-
Asal 5	7.1.1988	7.3.1987	2105	359	-	-
Asal 6	8.4.1988	10.6.1988	1761	280	150	130

The deposition products were varied and the scaling rate increased about six fold at a pressures below 16-bar g. The main products were:

- Sulphide at high pressures.
- Iron silicate at lower pressures (2 to 16 bar/g).
- Amorphous silica was the major deposit at a much lower pressure than the iron silicate.

During production, chemical deposition (scaling) took place in the well at differing rates with depth, the sulphide and the iron silicates are mostly deposited in the well but the silica mostly in surface equipment.

3. METHODOLOGY

3.1 Sampling methods

Surface exploration is the first step in locating and outlining geothermal fields. Application of geochemical methods during the various stages of exploration and evaluation of geothermal sources are particularly important (Óskarsson and Ármannsson, 2015). The collection of samples of non-boiling water can be divided into two categories, collection from natural springs and collection from hot water wells.

3.1.1 Sampling springs

The sampling of thermal fluid from springs, fumaroles or wells requires sampling equipment and possible chemical additives and care has to be taken during sampling. A sampling pump is usually used for sampling hot springs to make the collection of the water easy if it is not free flowing. The sampling is performed in the following way:

- Temperature, pH, conductivity and GPS coordinate measurements in the field are essential.
- Base is added to absorb acid gases, i.e. CO_2 and H_2S.
- Sample for silica (SiO_2) determination is diluted to prevent polymerization.
- Samples for the determination of anions and isotopes are filtered to prevent interaction with suspended matter.
- Samples for the determination of cations (including trace cations) are filtered too but also acidified to avoid adsorption on walls of containers.
- Sample for sulphate (SO_4) determination is filtered and sulphide precipitated.

3.1.2 Well Sampling

Samples from high-temperature wells may be collected from the wellhead or downhole. During collection from the wellhead the water and steam phases of the discharge are separated using the separator on the wellhead separating the whole discharge, or with a small Weber separator (pressure sampling) which is also used for the collection of samples from a two-phase pipeline (Figure 4). The inlet vent on the Weber separator is opened, the fluid is allowed to flow from the borehole through the separator, and for the sampling of the vapour phase, the water level inside the separator is kept low until preferably a mixture of water and steam flows through the water vent. For the collection of the liquid phase, the water level is kept high and ascertained that liquid water flows through the steam vent.
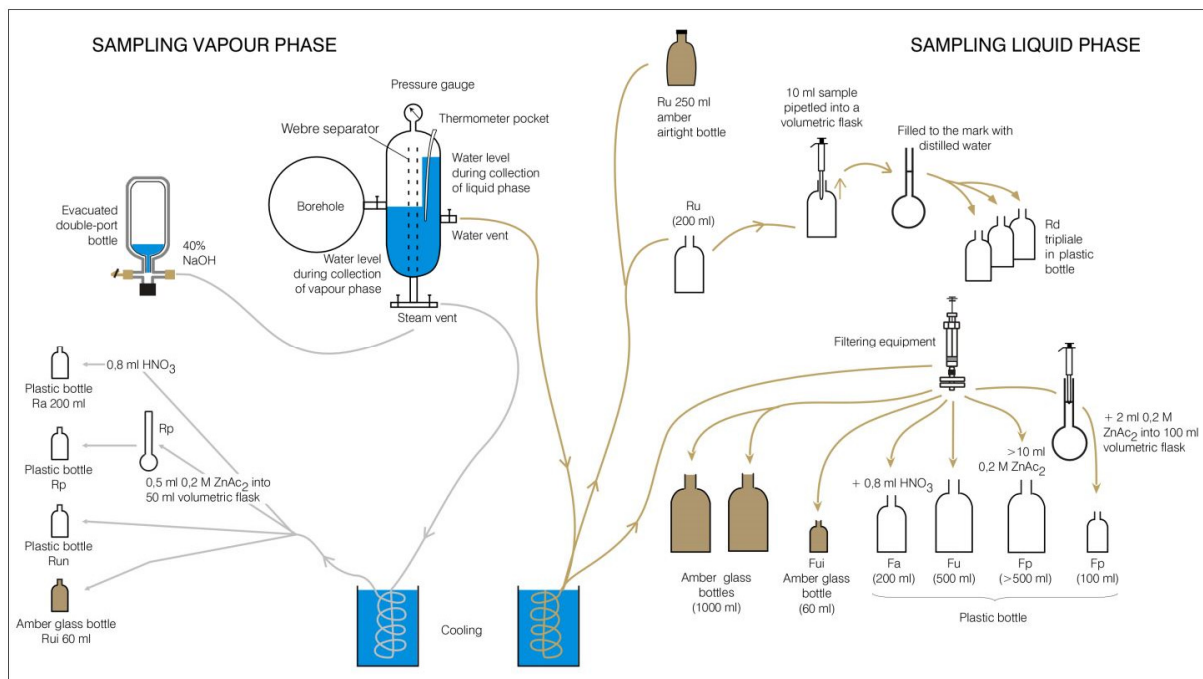

FIGURE 4: Sampling of wells (Ármannsson and Ólafsson, 2006)

3.2 Analytical methods

Samples of spring and well waters are analysed by various methods for different purposes. Although many geochemical, analytical and administrative considerations can influence the choice of an analytical method, sample preparation and determination are the principal analytical factors influencing the quality of the result. The analytical methods used are listed in Table 2.

3.3 Geothermometers

Geothermometers enable the temperature of the reservoir to be estimated using the chemical and isotope composition of hot spring water, fumarole discharges and well fluids. Geothermometers are probably the most important application of geochemistry in geothermal exploration and D'Amore and Arnórsson (2000) classified them into three groups as follows:

1) Water or solute geothermometers.
2) Steam or gas geothermometers.
3) Isotope geothermometers.

TABLE 2 : Analytical methods used (Sanjuan et al., 1990)

	ISERST	LGE*
Na	Flame emission	Atomic absorption
K	Flame emission	Flame emission
Li		Flame emission
Mg	Complexometry	Atomic absorption
Ca	Complexometry	Atomic absorption
Sr		Furnace atomic absorption
Cl	Titration	Ion chromatography
SO4		Ion chromatography
Br		Ion chromatography
B	Titration	Titration
Si		Colorim. (heptamolybdate)
Al	Titration	

* Laboratoire de Géochimie des Eaux "University Paris 7, Paris, France

The application of chemical geothermometers (water and steam) depends on mineral-fluid equilibria as well as the temperature at depth in the reservoir. This must be preserved during the passage of fluid from depth to the surface and it comprises the following assumptions (D'Amore and Arnórsson 2000):

- Fluid-mineral equilibrium at depth.
- A temperature dependent reaction at depth.
- An adequate supply of solid phases to permit the fluid to become saturated with respect to the constituents used for the geothermometer.
- Negligible re-equilibrium as the water flows to the surface.
- No dilution or mixing of hot and cold waters.

Many solute geothermometers have been developed, the silica (quartz and chalcedony), Na/K and Na-K-Ca geothermometers are the most important ones used, and will be described in the following chapters.

3.3.1 Silica geothermometers

The silica geothermometer is controlled by the solubility of different silica species as a function of temperature of the water. This can be studied with the different phases of silica, which are quartz, chalcedony, α- and β-cristobalite and amorphous silica. The solubility of each species depends on the pressure, temperature and the salinity of the water. The solubility reactions for silica minerals are invariably expressed as:

$$SiO_{2, (qtz)} + 2H_2O = H_4SiO_4^0 \tag{1}$$
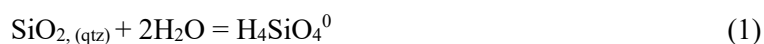
At a pH below 9, all silica is present as dissociated silicic acid $H_4SiO_4^0$ but at a higher pH a significant fraction has dissociated to $H_3SiO_4^-$. As the analytical result gives the total silica concentration but the geothermometer is based on the dissociated fraction, the dissociated fraction needs to be calculated and subtracted from the total to obtain the $H_4SiO_4^0$ fraction for geothermometry. Quartz is generally in equilibrium with the rock in solution at temperatures higher than 180°C but may be in equilibrium at considerably lower temperatures in old systems. The most used formula for the quartz geothermometer is valid if the quartz in the solution is in equilibrium with the rock at a temperature between 25 and 900°C (Fournier and Potter 1982):

$$T\ (°C) = -42.2 + 0.288315 \times S - 3.6686 \times 10^{-4} \times S^2 + 3.1665 \times 10^{-7} \times S^3 + 77.034 \times \log S \tag{2}$$

Chalcedony in the solution may be in equilibrium with the rock at temperatures up to about 180°C, although in old systems quartz may control the solubility down to 120°C or even lower. The two most common formulas for the chalcedony geothermometer are:

Fournier (1977) for 0-250°C:

$$T(°C) = \frac{1032}{4.69 - \log(SiO2)} - 273.15 \tag{3}$$

and Arnórsson et al. (1983a)

$$T(°C) = \frac{1112}{4.91 - \log(SiO2)} - 273.15 \tag{4}$$

Usually the chalcedony geothermometer is valid up to about 120°C and the quartz above 180°C, at temperatures between 120°C and 180°C conditions such as the age of the system may be used to determine which geothermometer to use.

In low pH waters such as CO_2 rich waters (<50°C), amorphous silica may control the solubility. Fournier presented the following formula for such cases and it is valid for equilibrium at 25-250°C (Fournier, 1977):

$$T(°C) = \frac{731}{4.52 - \log(SiO2)} - 273.15 \tag{5}$$

3.3.2 Cation geothermometers

Cation geothermometers (e.g. Na/K and Na-K-Ca) are used to estimate the reservoir temperature due to the dependence on the equilibrium between the geothermal fluids and the minerals of the reservoir such as alkali feldspars. The exchange reactions between the alkali feldspars with sodium (Na) and potassium (K) are represented as follows:

$$\begin{array}{ccc} NaAlSi_3O_8 + K^+ \longleftrightarrow & KAlSi_3O_8 + Na^+ \\ (Albite) & (K\ feldspar) \end{array} \tag{6}$$

For the feldspars, the equilibrium constant is simply (the activity of the feldspar species is ~ 1):

$$K_{alkali\ field} = \frac{[Na+]}{[K+]} \tag{7}$$

Some formulas that are used to calculate the reservoir temperature using the Na-K geothermometer are: Fournier (1979):

$$T°C = \frac{1217}{1.438 + \log(\frac{Na}{K})} - 273.15 \tag{8}$$

Arnórsson et al. (1983a):

$$T°C = \frac{933}{0,993 + \log(\frac{Na}{K})} - 273.15 \qquad\qquad 25\text{-}250°C \tag{9}$$

Giggenbach (1988):

$$T°C = \frac{1390}{1.750 + \log(\frac{Na}{K})} - 273.15 \tag{10}$$

Concentrations are in mg/kg

Fournier and Truesdell (1973) developed the Na-K-Ca geothermometer. It is used not only for the calculation of the reservoir temperature but it also takes into account the calcium concentration which, especially in cold and slightly thermal, non-equilibrated water, may affect the Na/K geothermometer.

Fournier and Truesdell (1973):

$$T°C = \frac{1647}{\log\left(\frac{Na}{K}\right) + \beta \log\left(\frac{\sqrt{Ca}}{Na}\right) + 2.24} - 273.15 \tag{11}$$

Concentrations are in mol/kg. $\beta = 4/3$ for $t < 100°C$ and $1/3$ for $t > 100°C$ and for log (Ca0.5/Na) < 0.

3.4 The Cl-SO₄-HCO₃ ternary diagram

For the interpretation of geothermal water data, Giggenbach (1991) suggested that the Cl-SO₄-HCO₃ ternary diagram (Figure 5) is useful as an initial classification in terms of the major anions Cl, SO₄ and HCO₃, partly because most ionic solute geothermometers work best in neutral or mature waters with high Cl and relatively low HCO₃ concentrations.

The sum of the concentrations of the three constituents (such as Cl, SO₄ and HCO₃) in ppm (mg/kg), allows the construction of a triangular plot. In the present case:
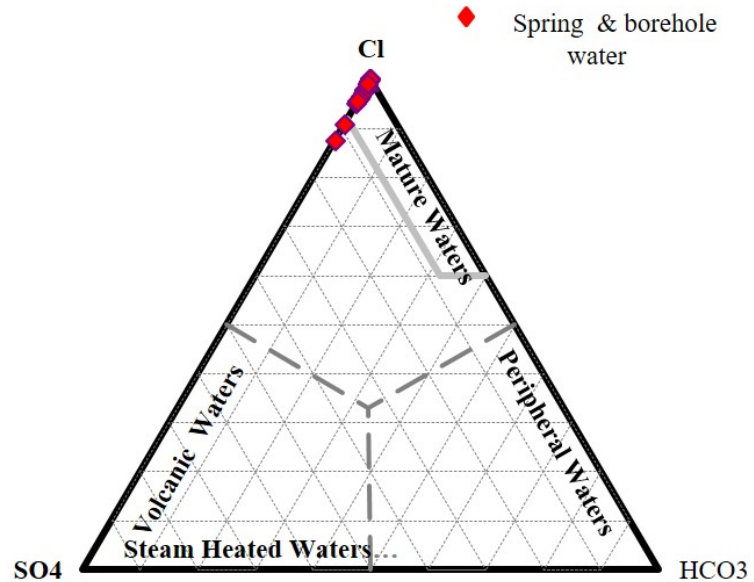
FIGURE 5: Classification of the thermal water and the well water using the Cl-HCO₃-SO₄ ternary diagram

$$S = C_{Cl} + C_{SO4} + C_{HCO3} \tag{12}$$

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

$$\text{"%-Cl"} = 100c_{Cl}/S \tag{13}$$

$$\text{"%-SO4"} = 100c_{SO4}/S \tag{14}$$
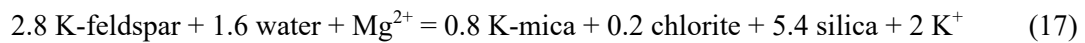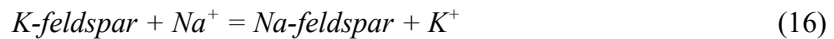
$$\text{"%-HCO3"} = 100c_{HCO3}/S \tag{15}$$

Chloride is commonly discharged from hot springs and it is a conservative ion in the geothermal fluid, which means that it does not take part in reactions with rocks after dissolution with the water. Thus, the chloride is used as a tracer in geothermal investigations. An example of the use of a Cl-SO4-HCO3 ternary diagram is presented in Section 4.1.1.

3.5 The Na-K-Mg ternary diagram

As the triangular shape Cl-SO₄-HCO₃ ternary diagram, the evaluation of the Na, K and Mg is best represented by the use of the blank diagram provided by Giggenbach (1988). This ternary diagram is divided into three different areas according to which the water is classified (Figure 6):

- Immature water.
- Partial equilibrium.
- Full equilibrium.

The positions of the Na, K and Mg concentrations in the ternary diagram depend on the temperature. It is essentially based on the temperature dependence of two reactions:
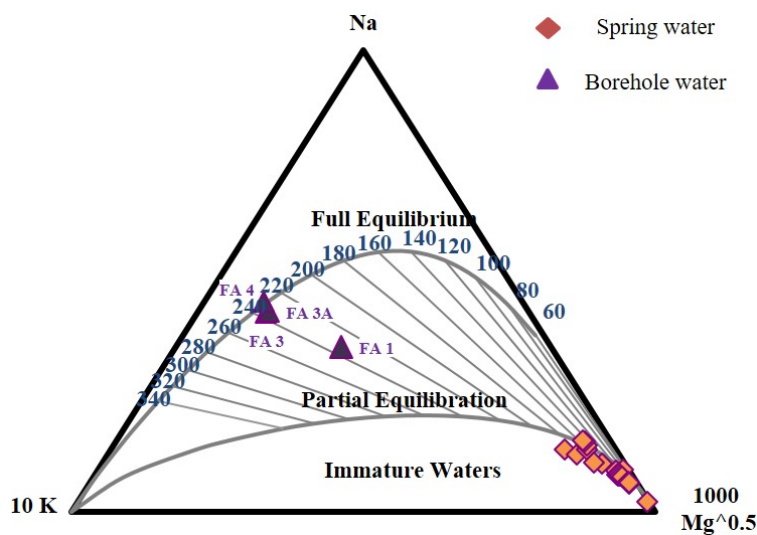
$$K\text{-}feldspar + Na^+ = Na\text{-}feldspar + K^+ \tag{16}$$

$$2.8 \text{ K-feldspar} + 1.6 \text{ water} + Mg^{2+} = 0.8 \text{ K-mica} + 0.2 \text{ chlorite} + 5.4 \text{ silica} + 2 \text{ K}^+ \tag{17}$$

The position of the data point in the Na-K-Mg ternary diagram is obtained by establishing the sum of the concentrations "%-Na'', "%-K'' and "%-Mg'' involved:

$$S = C_{Na}/1000 + C_k/100 + \sqrt{C_{Mg}} \tag{18}$$

$$\text{"%-Na''} = C_{Na}/10S \tag{19}$$

$$\text{"%-K''} = C_K/S \tag{20}$$

$$\text{"%-Mg''} = 100\sqrt{C_{Mg}}/S \tag{21}$$

Among the well and the spring discharges, the shift in K-Mg temperature is also dependent on the time taken by the water to move from depth to the surface. An example of the use of a Na-K-Mg ternary diagram is presented in Chapter 4.1.2.

FIGURE 6: The Na-K-Mg ternary diagram for samples of the thermal water and well water from the study area

3.6 Mixing models

Geothermal water is prone to mixing with cold water after a variable amount of conductive cooling has taken place and where there is a change in permeability. Since cold waters are normally lower in dissolved solids than geothermal waters, mixing is quite often referred to as dilution. According to Arnórsson (2000), mixing models have been been developed to allow the estimation of the hot water component in mixed waters emerging in springs or discharged from shallow drill holes. Besides, mixing models also provide a useful check before geothermometer calculations are carried out., Three kinds of mixing models that have been applied in geothermal exploration are:

1) The chloride-enthalpy mixing model.
2) The silica-enthalpy warm spring mixing model.
3) The silica-carbonate mixing model.

The application of mixing models to well discharge is useful for monitoring changes in its composition particularly during the early stages of discharge., e.g. for establishing the diminishing proportion of drilling fluids and thus the real geothermometer temperature of the reservoir fluid. Such information may be more useful to establish the reservoir temperature than logging.

The chloride-enthalpy mixing model is useful to estimate the temperature of the hot water component of the flow from boiling hot springs, particularly when the initial reservoir temperature is above 200°C (Fournier, 1977). However, it has to be established that the chloride concentrations of the hot and cold fluid components are different as chloride is a conservative component not dependent on water-rock equilibrium.

The silica-enthalpy diagram makes the estimation of the temperature of the hot-water component of mixed waters possible. This method is based on the relation between the equilibrium concentration of silica dissolution and heat and its successful application is dependent upon three basic assumptions (Fournier and Truesdell, 1973; Truesdell and Fournier, 1977; Nicholson, 2012):

- There is no loss of heat after mixing.
- The solubility of quartz (or chalcedony) controls the silica concentration of the reservoir fluid.
- There is no deposition of silica once the geothermal fluid has left the deep reservoir, before or after mixing.

The silica-carbonate mixing model is based on the relationship between dissolved silica and total carbonate ($\sum CO_3$) equilibrium concentrations in geothermal fluids. This model is useful to estimate the temperature of the reservoir when the mixing prevents boiling, and to distinguish between boiled and non-boiled waters (Arnórsson, 1985).

4. RESULTS AND DISCUSSION

The results of the water analysis of 28 samples in the Asal-Ghoubbet area, of which 22 samples were collected from springs and six samples from the Asal wells, are presented in Table 3. These results show that all the samples have a higher salinity than that of seawater like the thermal water samples from Lake Asal, except samples K1 and K2 from Kalou Wadi, which have a low salinity. Measured surface water temperature varies between 30-90°C for the thermal water and the well reservoir temperature from 260°C to more than 280°C.

4.1 Classification of the samples

4.1.1 The Cl-SO$_4$-HCO$_3$ ternary diagram

The construction of this ternary diagram which includes the major anion concentrations of the waters (Cl-HCO$_3$-SO$_4$) makes it possible to classify the waters according to their origins, such as mature waters, peripheral waters, steam heated waters and volcanic waters (Giggenbach, 1988), and thus identify individual samples. The results of the analysis of the hot spring water and well samples from the Asal area show that chloride is the predominant anion (Figure 7). This allowed some of the waters to be classified as mature waters and some as volcanic waters. Thus, there is water-rock interaction resulting in relatively high chloride concentrations and some possible volcanic influence leading to relatively high sulfate concentrations.

4.1.2 The Na-K-Mg ternary diagram

The main purpose of Giggenbach's (1988) ternary diagram is to determine the reservoir temperature on the basis of the Na-K and K-Mg geothermometers, but an important aspect is its utilization to infer the equilibrium state of these ions in the water with respect to equilibration with the rock. From Figure 8 it is clear that the water from the warm and hot springs in the Asal-Ghoubbet area plot as immature waters with a relatively high magnesium concentration, suggesting a high proportion of cold groundwater. On the other hand, the fluids from the Asal wells plot close to the full equilibrium line except that from well

Asal 1, which plots as a partially equilibrated water. The reservoir temperature is thus in the range 220-260°C.

TABLE 3: Chemical analysis of water from the Asal-Ghoubbet region (results in millimoles/liter)

Source		T (°C)	pH	Na	K	Ca	Mg	Li	Sr	Cl	SO₄	Br	B	SiO₂	$^{87}Sr/^{86}Sr$
Korilii	**AS 1**	80	-	427	11.5	77.2	18.4	0.38	0.56	640	2.63	1	0.34	1.05	0.70449
Manda	**AS 2**	40.5	7.14	682	19.5	39.2	62.6	0.2	0.3	840	19	1.55	0.53	0.42	0.70599
	AS 3	45	7.07	713	21.4	55.7	66.2	0.23	0.37	940	19	1.76	-	0.74	0.70577
	AS 4	43	7.26	680	20.5	42	56	.	.	820	-	-	-	1.04	-
	AS 5	45	7.3	670	19.2	38	56.8	0.08	.	810	-	-	0.55	1.21	-
	AS 9	38.5	7.45	675	19.9	43.1	60.6	0.12	0.19	839	30.2	1.53	0.56	1.35	0.7066
	AS 10	30	7.2	535	11.4	14	61	0.046	0.1	617	32	1.09	0.39	0.52	0.70862
Eadkorar	**AS 6**	84	-	820	52.4	242	22	1.36	0.62	1395	0.1	2.9	0.65	1.38	0.70435
	AS 7	90	-	789	46	211	25.9	1.28	1.19	1330	0.1	2.73	0.65	1.37	0.7036
Eounda Alifitta	**AS 8**	39	-	3700	138	180	500	-	-	5120	-	-	2.2	0.15	-
	AS 11	58.5	6.48	609	22.5	15.2	24.8	-	-	974	26.3	1.9	0.65	1.1	-
	AS 12	-	-	-	-	-	-	-	-	815	-	1.55	0.58	-	0.70679
Kalou Wadi	**K1**	74	-	31.9	0.315	3.2	0.1	0.0079	0.016	31.6	3.17	0.07	0.17	1.33	0.70403
	K2	35	-	24	0.345	5.64	1.11	0.0035	0.024	28.3	3.99	0.05	0.07	0.49	0.70574
	K4	-	-	710	18.4	75.2	59.7	0.37	0.37	1070	3.57	2.04	0.51	-	0.70486
	K5	-	-	600	15.3	73.5	46.8	0.37	0.48	880	3.62	1.69	0.49	-	0.70481
	K6	-	-	550	12.9	74.5	41.6	0.36	0.51	830	3.07	1.56	0.46	-	0.70456
Ghoubbet	**G1 (sea)**	-	-	497	11.2	10.2	57.5	0.37	0.096	594	27.4	1.01	0.44	0.02	0.70903
	G2	60	-	490	10	20.6	48.2	0.72	0.165	588	23.9	1.01	0.47	0.32	0.70700
Lake Asal	**S1**	-	-	3565	111	63.7	403	0.70	0.74	4600	-	8.11	-	-	0.70645
	S2	32	7.1	4120	121	61.6	472	0.67	0.60	5190	44.8	-	2.96	-	-
	S3	32	7.0	4400	132	66.8	514	0.80	0.75	5610	45.8	-	2.99	-	-
Boreholes	**FA 1**	255	-	1240	125	409	0.97	1.87	-	2200	0.22	-	0.6	8.55	0.70424
	FA 3	260	4.65	1142	120	385	0.1	2.04	2.3	2033	0.20	3.71	0.73	-	0.70439
	FA 3A	-	5.22	1115	115	356	0.1	-	-	1970	-	-	0.65	-	-
	FA 4	-	5.13	1400	136	437	0.1	2.2	1.75	2400	0.28	-	0.65	-	0.70426
	NA 3 (419m)	100	7.8	513	24.8	77.1	16.3	0.6	0.45	798	6.81	-	0.43	1.74	0.70463
	NA 4 (255m)	33	8.15	510	10.6	13.1	55.4	0.04	0.095	590	27.9	0.98	0.39	0.32	0.7088

4.2 Solute geothermometers

Various chemical geothermometers like quartz (Fournier and Potter, 1982), chalcedony (Arnórsson et al., 1983a), Na-K (Arnórsson et al., 1983a) and Na-K-Ca (Fournier and Truesdell, 1973) have been used to calculate the reservoir temperature in the Asal-Ghoubbet area as described in Chapter 3.3. The results of these calculations and the surface temperature measurements are presented in Table 4. For quartz, the calculated temperature ranges between 34-261 °C, with the lowest temperatures being found for sample AS8 from Eounda Alifitta and the highest temperature for the sample from the well Asal 1. As expected, the lowest and the highest chalcedony temperatures are found for AS8 spring water (8°C) and the fluids from Asal 1 (232°C), with 0.15 mmol/l and 8.55 mmol/l silica concentration respectively. For the Na-K-Ca geothermometer, the temperature varies between 107 and 269°C and the temperature ranges between 64 and 263°C for the Na/K geothermometer. These results are also shown in the form of a diagram in Figure 7.
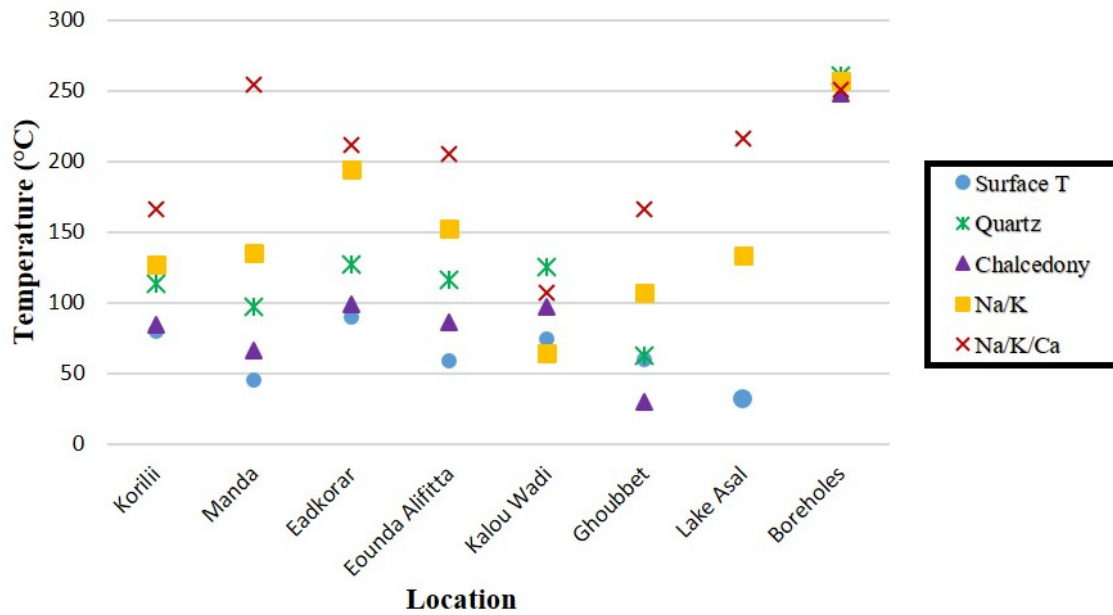
FIGURE 7: Results of temperature calculations with silica, Na/K and Na-K-Ca geothermometers
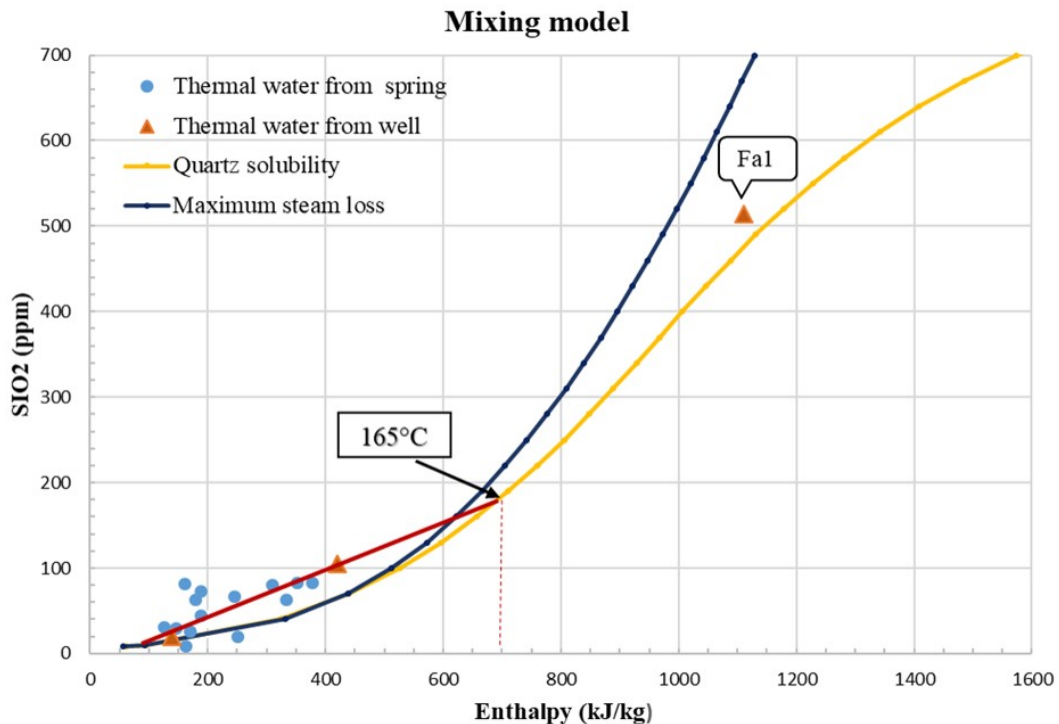and measured spring and well temperatures

FIGURE 8: Silica-enthalpy mixing model for springs and borehole water
from the Asal-Ghoubbet area

Most of the silica geothermometer temperatures estimated for the spring samples from the Asal-Ghoubbet area are below 120°C and thus the silica concentration is most likely controlled by equilibrium with chalcedony. In some cases, the silica concentration might be controlled by equilibrium with quartz, either because the rock is old or because mixing with cool groundwater might have taken place. For the quartz geothermometer temperature for the Asal well water the temperature is estimated to be above

TABLE 4: Measured surface temperature and the results of reservoir temperature calculations by
solute geothermometers for the samples of spring waters and borehole waters in
Asal-Ghoubbet, Djibouti

Samples	T surface (°C)	T Quartz [1] (°C)	T Chalcedony [2] (°C)	T Na/K [3] (°C)	T Na/K/Ca [4] (°C)	T Na/K/Ca (°C) after correct.
*Korili*ï						
AS 1	80	113	84	127	166	96
Manda						
AS 2	40.5	73	44	131	264	34
AS 3	45	97	68	135	254	37
AS 4	43	113	84	136	264	43
AS 5	45	120	92	132	264	35
AS 9	38.5	126	97	134	260	31
AS 10	30	82	52	110	269	n.a.
Eadkorar						
AS 6	84	127	99	204	217	177
AS 7	90	127	98	194	212	147
Eounda Alifitta						
AS 8	39	34	8	153	218	n.a.
AS 11	58.5	116	87	152	205	55
AS 12	-	-	-	-	-	-
Oued Kalou						
K1	74	125	97	64	107	107
K2	35	79	50	85	115	98
K4	-	-	-	124	173	43
K5	-	-	-	123	170	48
K6	-	-	-	117	164	52
Ghoubbet						
G2	60	62	34	107	166	n.a.
Lac Asal						
S1	-	-	-	138	217	n.a.
S2	32	-	-	133	216	n.a.
S3	32	-	-	135	218	n.a.
Boreholes						
FA 1	255	261	232	257	251	251
FA 3	260	-	-	263	253	253
FA 3A	-	-	-	260	252	252
FA 4	-	-	-	252	251	251
NA 3 (419m)	100	140	112	176	202	137
NA 4 (255m)	33	62	34	109	171	171

1) Fournier and Potter, 1982 (25-900°C); 2) Arnórsson et al., 1983a; 3) Arnórsson et al., 1983a (25-250°C); 4) Fournier and Truesdell, 1973; n.a.: not applicable

180°C and thus the silica solubility is controlled by equilibrium with quartz, and the Na/K temperature is similarly in agreement with the measured temperature. For most samples, the Na/K geothermometer suggests temperatures well below 180°C and supports the use of the chalcedony geothermometer. The Na-K-Ca geothermometer gives higher temperatures for the samples compared with the Na/K geothermometers, suggesting a lack of equilibrium with rock minerals or high Mg concentrations. According to Fournier and Potter (1979), the higher Mg^{2+} concentrations indicate that water-rock reactions have taken place at a relatively low temperature. The thermal waters from Manda and Lake Asal have high estimated Na-K-Ca temperatures and high Mg^{2+} concentrations but the measured surface temperature is eventually lower.

A method of applying a magnesium correction to Na-K-Ca estimated temperature was applied when the data was plotted as shown in Appendix I (Figure 1). The results for the magnesium correction to the Na-K-Ca chemical geothermometer are demonstrated in Appendix I (Table 1).

4.3 Mixing models

The line that passes through the data points cuts the quartz solubility curve at a point of intersection (Figure 8). This point of intersection has the enthalpy value 700 kJ/kg of the hot water in the mixted water and 165°C as the temperature from steam tables. Thus, the temperature of the hot water component before mixing with cold groundwater in the Asal-Ghoubbet area is 165°C.

The estimated temperature of the Asal region aquifer using this method is particularly high compared to the result of the calculated quartz geothermometer temperature presented in Table 4 and Figure 7. This may infer that most of geothermal hot spring water was mixed with cold water and there has been an infiltration of cold water into the reservoir.

The liquid component of the fluid from well Asal 1, whose silica concentration and enthalpy are high or 513.8 mg/kg and 1100 kJ/kg respectively, was probably not mixed with cold water, because the temperature estimated for 1100 kJ/kg enthalpy of the hot water in mixed water using a steam table is 255°C, which is about the same as the calculated quartz temperature (260°C) and measured temperature (255°C).

4.4 Origin of the water

The ratios of isotopes such as those of oxygen (^{18}O and ^{16}O) and hydrogen (^{2}H and ^{1}H,) and the correlation between Boron (B) and Chloride (Cl) are important tracers in identifying the origin of geothermal fluids.

4.4.1 Isotopes

When isotope ratios are used to trace the origin of geothermal water, it is important to realise that although the isotope values suggest the origin, processes such as mixing, water-rock interaction, condensation and age may have to be accounted for (Óskarsson and Ármannsson, 2015).

The isotope analysis of water from well Asal 3 was carried out by Virkir-Orkint (1990) and the value of $\delta^{18}O$ is 0.92‰. Fontes et al. (1979) and Fouillac et al. (1983) carried out the analysis for the oxygen and hydrogen isotope ratios of water from the Asal-Ghoubbet area and they classified the thermal springs into three groups with reference to these ratios (Sanjuan et al. 1990):

1) The Korilii group which is located on the south of the lake with the lowest mineralization and resembling seawater. The oxygen and hydrogen isotope data indicate a meteoric contribution.
2) The Northeast group from the lake (Eadkorar) involving thermal waters whose source of water is meteoric and highly saline. The higher salinity was acquired by the leaching of evaporates and the chemical composition by interaction with the reservoir rock.
3) The thermal springs of Manda are located in the central zone of the rift. The origin of the water is seawater, which reaches the lake via fissures.

Having classified the thermal water, they propose three hypotheses on the possible origin of the geothermal fluids as follows:

1) Leaching of evaporites, a mixture of seawater and current meteoric water is in equilibrium with reservoir rocks.

2) A mixture of meteoric water, seawater and a small proportion of Lake Asal water is in equilibrium with reservoir rocks.
3) Old meteoric water is in equilibrium with the reservoir rock after the leaching of the salt deposit.

The interpretation of previous results suggests that the main processes that influence the chemical composition of the Asal-Ghoubbet fluids are: infiltration of seawater, evaporation, the dissolution of evaporites and the water-basalt interaction at high temperatures.

4.4.2 Cl/B Ratio

The correlation between boron (B) and chloride (Cl) is used to trace the geothermal water's mixing with seawater or magmatic steam with precipitation but also the mixture of evaporated water. The reason is that the boron concentration of seawater and thus precipitation is low, but that of rocks and volcanic steam is much higher. On the other hand, the chloride concentration of seawater is high but that of rocks and volcanic steam low (Óskarsson and Ármannsson, 2015).

The relation between Cl and B in Figure 9 shows that those with values close to the line are seawater that has undergone some water-rock interaction. Those with Cl values close to zero are groundwater (or surface water) samples that have also taken up some B during water-rock interaction. The blue dots with very low B values are likely to be seawater that has evaporated to a different extent but not undergone water-rock interaction. For the samples from Lake Asal (S1, S2, and S3) and AS8 with very high chloride and moderate B concentrations are likely to have taken part in some water-rock interaction and then evaporated. The samples from the well with a B concentration close to zero and a high Cl concentration compared to the seawater have probably evaporated.
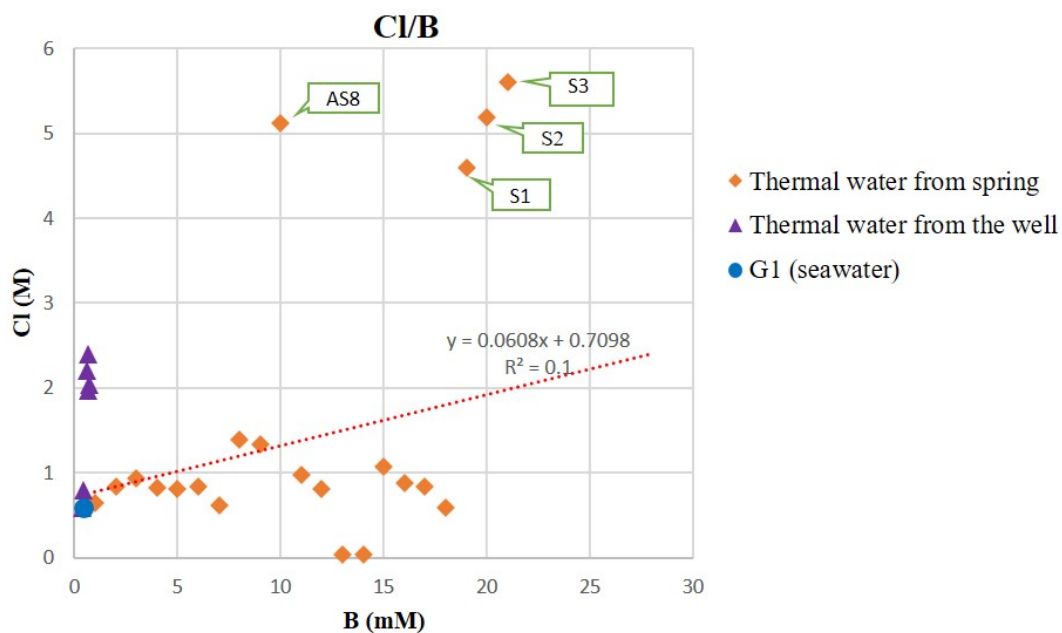
FIGURE 9: Relation between Cl and B for thermal water from springs and borehole water from the Asal-Ghoubbet area

5. CONCLUSIONS

Interpretation of the thermal fluid chemistry of the Asal-Ghoubbet region was carried out by examining the correlation between the major ion concentrations, boron, and silica concentrations, and enthalpy, and mixing to estimate the reservoir temperature using geothermometers and establish the origin of the water.

The chemical analysis of 28 samples of which 22 samples were collected from springs, seawater and lake water, and six samples from Asal wells was used for geochemical interpretation of the thermal water in this area.

Classification of the samples using the Cl-SO$_4$-HCO$_3$ ternary diagram suggests that their chemical composition is derived from water-rock interaction but influenced by volcanic water with high chloride and sulfate concentrations. According to the Na-K-Mg ternary diagram, the spring waters, lake and sea water are likely to have mixed with cold groundwater or be immature waters that have not attained equilibrium with the rock as can be deduced from their high magnesium concentrations. However, the borehole waters plot as mature waters that have equilibrated with the rock at 220-260°C.

Reservoir temperature estimation using solute geothermometers indicates that the silica concentration of the spring samples is controlled by equilibrium with chalcedony because the calculated source temperature is below 120°C. Those are not controlled by equilibrium with quartz because the rock is probably not old enough or the water has mixed with cool groundwater. The Na/K geothermometer suggests temperatures well below 180°C and supports the use of the chalcedony geothermometer. On the other hand, a higher temperature estimate for the Na-K-Ca geothermometer may be caused by equilibrium with rock minerals or show immature cool waters as indicated by high Mg concentrations. For the fluids of the Asal wells, the geothermometer temperature calculated is in agreement with the measured temperature and the silica concentrations are controlled by equilibrium with quartz.

Using the silica-enthalpy mixing model, the temperature of the hot water component before mixing with cold groundwater is 165°C in this area. This temperature is higher than the temperature calculated using the quartz geothermometer. Thus, the water from the springs was mixed with cold groundwater, while water from well Asal 1 has not mixed with cold water and the estimated temperature of the hot water reservoir is 255°C.

The correlation between Cl and B concentrations suggests that most of the thermal water has undergone water-rock interaction, apart from the well waters and the evaporated seawater sample. The waters from the Lake Asal samples and AS8 from Eaounda Alifitta are probably waters that have evaporated after water-rock interaction.

Finally, the composition of the thermal waters in the Asal-Ghoubbet area was interpreted considering a combination of water-rock interaction and evaporation of the solution. The conclusion was that the waters sampled have not equilibrated with reservoir rock, except the fluids from the wells. According to Sanjuan et al. (1990), the superficial circuits are not in direct contact with the fluids of the reservoir like the fluids encountered in the Asal wells. Supposedly, there is no contact, or the contact is limited and then there is re-equilibration.

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APPENDIX I: SUGGESTED CORRECTION PROCEDURE

1. Calculate the Na-K-Ca temperature as described by Fournier and Truesdell (1973). Do not apply a magnesium correction if this calculated temperature is below 70°C.

2. Calculate R= {Mg/ (Mg + Ca + K)} * 100, using equivalent units of concentration.

3. If R > 50, assume that the water comes from a relatively cool underground environment at a temperature approximately equal to the measured water temperature, irrespective of high calculated Na-K-Ca temperature.

4. If the calculated Na-K-Ca temperature is greater than 70°C and R< 50, use Figs 4, 6, or 7 to calculate Δt_{Mg}, which is the temperature correction (in °C) to be subtracted from the Na-K-Ca calculated temperature.

5. When using a computer to calculated Δt_{Mg} the following tests should be included in the program:
   a) Check if the Na-K-Ca calculated temperature is > 70°C. if yes, do not proceed further with a magnesium correction.
   b) Check if R> 50. If yes, assume that the water in the aquifer is relatively cold and do not proceed further with a magnesium correction.
   c) If R = 5-50, use eqn (1) to calculate Δt_{Mg}. Do not apply a magnesium correction if Δt_{Mg} is negative.
   d) If 0.5 < R < 5, use eqn (2) to calculate Δt_{Mg}. Do not apply a magnesium correction if Δt_{Mg}. Do not apply a magnesium correction if Δt_{Mg} is negative, or if R < 0.5.
   e) Subtract Δt_{Mg} from the calculated Na-K-Ca temperature.

TABLE 1: The results of the magnesium correction to the Na-K-Ca chemical geothermometer
of Asal-Ghoubbet area

| Samples		T surface (°C)	T Na/K/Ca (°C)	R	Δt_{Mg}	T Na/K/Ca (°C) after correction
Korilii	AS 1	80	166	15,51	70	96
Manda	AS 2	40,5	264	44,46	230	34
	AS 3	45	254	40,19	217	37
	AS 4	43	264	40,29	221	43
	AS 5	45	264	42,64	229	35
	AS 9	38,5	260	42,23	229	31
	AS 10	30	269	62,37	**R > 50**	n.a.
Eadkorar	AS 6	84	217	5,97	40	177
	AS 7	90	212	7,87	65	147
Eounda Alifitta	AS 8	39	218	52,30	**R > 50**	n.a.
	AS 11	58,5	205	29,18	150	55
	AS 12	-	-			
Oued Kalou	K1	74	107	2,54		107
	K2	35	115	14,92	17	98
	K4	-	173	34,77	130	43
	K5	-	170	31,01	122	48
	K6	-	164	29,32	112	52
Ghoubbet	G2	60	166	54,28	**R > 50**	n.a.
Lac Asal	S1	-	217	58,52	**R > 50**	n.a.
	S2	32	216	60,86	**R > 50**	n.a.
	S3	32	218	60,84	**R > 50**	n.a.
Boreholes	FA 1	255	251	0,15	**R < 0.5**	251
	FA 3	260	253	0,02	**R < 0.5**	253
	FA 3A	-	252	0,02	**R < 0.5**	252
	FA 4	-	251	0,01	**R < 0.5**	251
	NA 3 (419m)	100	202	11,40	65	137
	NA 4 (255m)	33	171	61,76	**R > 50**	171

n.a.: not applicable
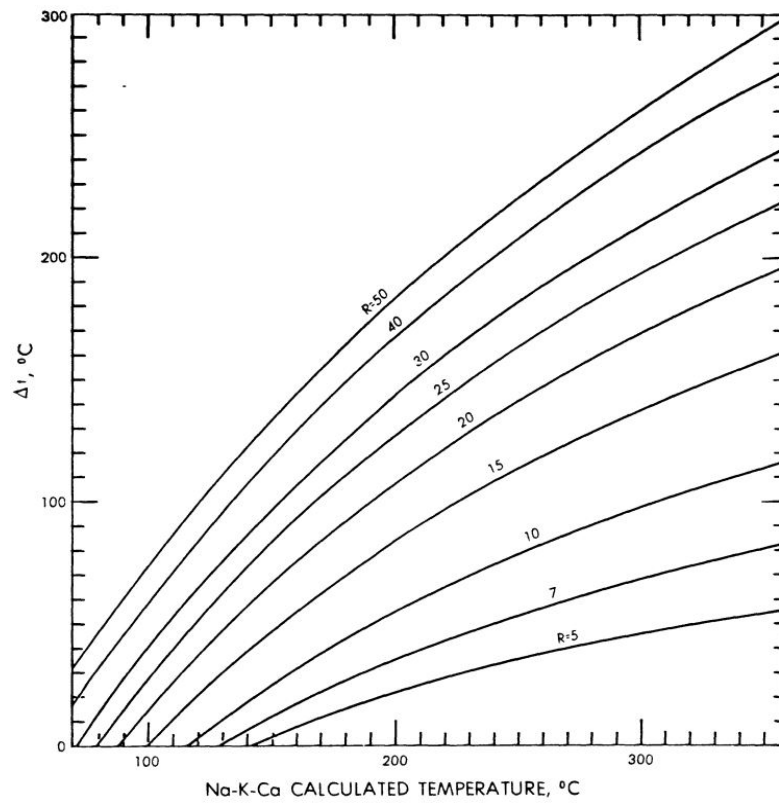
FIGURE 1: Magnesium correction to the Na-K-Ca chemical geothermometer