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# GEOCHEMISTRY OF THERMAL WATERS FROM AL-LISI – ISBIL GEOTHERMAL FIELD, DHAMAR GOVERNORATE, YEMEN

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### ABSTRACT

The Al-Lisi – Isbil geothermal and volcanic field, one of Yemen's important fields, is known for its fumaroles, steaming grounds and hot wells. The area is mainly composed of basaltic lava flows, stratified basic tuffs and agglomerate pyroclastics. Less common are differentiated rock-types like rhyolite. The Al-Lisi volcano is though an exception which consists entirely of acidic lava flows (rhyolite, obsidian, acidic tuffs and ash rings). Chemical analyses from 29 shallow water wells from the Al-Lisi – Isbil area were reviewed. All the data were interpreted using the WATCH program for speciation and by mineral equilibrium diagrams and other graphical presentations and classifications. The maximum reservoir temperature for the wells, predicted by calculation of various geothermometers, exceeds 100°C. There is evidence of mixing with cold water. The thermal fluid is of bicarbonate type and the reservoir rocks consist mainly of sandstone (Tawilah Formation) at 1000 to 1500 m depth.

#### **1. INTRODUCTION**

The Al-Lisi – Isbil volcanic and geothermal field is located approximately in the mid eastern part of the Dhamar governorate in central western Yemen, about 80 km south of the capital Sana'a (Figure 1). Numerous boreholes for agricultural purposes have been drilled in the area and most of them contain thermal water with temperatures ranging from  $21^{\circ}$ C to  $59^{\circ}$ C and pH values between 6.3 and 9.1. Chemical analyses have been done for the samples collected from the hot water wells, discharging from Tertiary-Quaternary igneous rocks. Temperatures and pH were measured directly in the field. Furthermore, there are anomalous fumaroles (Al-Lisi) and steaming grounds (Isbil) that have low pH values (< 4.5) and TDS (< 250 ppm). This report presents chemical data obtained from 29 thermal and cold wells in the area. The sampling was carried out in 2007, based on the scientific collaboration between the Geological Survey and Mineral Resources Board of the Ministry of Oil, Yemen and the Department of the Earth Sciences and the National Council of Research (CNR) – Study Center for Mineralgenesis and Applied Geochemistry of Florence, Italy.

The Republic of Yemen has a strategic position among the Middle East's countries. It is located on the south Arabian Peninsula, between latitudes 12 and 20°N, and between longitudes 41 and 54°E, and the total area is 527,970 km<sup>2</sup>. Yemen consists of 21 Governorates. The Dhamar Governorate is in the middle of west Yemen. The Al-Lisi – Isbil volcanic area is located about 15 km east of Dhamar city. The study area is within 44°23' and 44°46' E and 14°26' and 14° 41'N, and covers approximately 740  $\text{km}^2$  (Figure 1).

### 2. BACKGROUND AND PREVIOUS STUDIES

Report 10

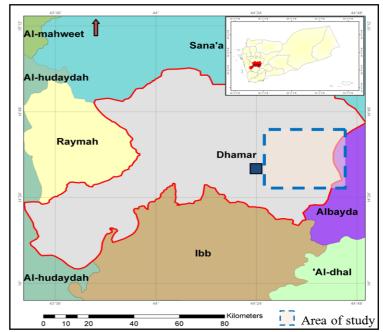


FIGURE 1: Location map of the Al-Lisi - Isbil area, east of Dhamar city in Yemen; the area of the present study is within the dashed box

The western Yemen volcanic province is characterized by several

hydrothermal features, such as thermal springs, condensates, fumaroles and in many cases hot well waters. These thermal features are related to relatively shallow felsic magma chambers (Mattash, 1994). The location of Yemen is thought to be at one of the most active plate boundaries of the World, i.e. the triple junction made up by the Gulf of Aden, the Red Sea and the Eastern African Rift System. Alkaline flood basalts of the Yemen trap series (YTS) occupy about 50,000 km<sup>2</sup> of the central-western sector of Yemen and are Oligocene to Quaternary in age. Recent volcanic activity is present in several areas, such as that which occurred near Dhamar, where a volcanic eruption was described in 1937 (Plakfer et al., 1987). As a consequence of thermal equilibrium between the upper mantle and the crust, anomalous upflow of heat started in Yemen at about 40 Ma, and reached its maximum at about 12 Ma (Elf Aquitaine, 1990 - in Mattash, 1994).

The present geothermal gradient in the Red Sea region is still quite anomalous, varying from 49 to  $77^{\circ}$ C/km, with relative heat flow ranging from 94 to 154 mW/m<sup>2</sup>. As a result of volcanism, anomalous heat flow and related hydrothermal circulation, relatively large epithermal alteration haloes are present in many places, such as the opalitic alteration around the Quaternary Al Lisi volcano (Mattash et al., 2001). The thermal water discharges of Yemen are highly variable in composition, due to different origins and water-rock-gas interaction processes. The majority of thermal springs and gas vents are associated with the Western Yemen Cenozoic volcanic province. Structurally, they are connected to north-northwest trending linear faulting that is parallel to the main Red Sea trend, and partially connected to Tertiary felsic intrusions. Several Quaternary to recent volcanic cones, domes, craters, (such as in the Al-Lisi -Isbil area) and collapsed calderas are also characteristic geologic and structural features. The high mineral contents of some thermal waters are believed to have medicinal properties (Minissale et al., 2007).

From a classification point of view, the waters of the Dhamar area have a Na(K)-Cl composition, the Al-Lisi and Isbil volcanoes are of Na-HCO<sub>3</sub> type with discharges often associated with CO<sub>2</sub>-rich gas phase, increasing the water-rock interaction processes. This may lead to a higher degree of alteration, and favouring ion-exchange reactions with Na-rich silicates, these waters thus become Na-HCO<sub>3</sub> in composition (Mattash et al., 2001). The source of heat can be indicated in some Quaternary volcanic fields (e.g. Dhamar-Rada'a) from the relatively elevated water temperatures of hot springs and also from many drilled wells, which in turn suggests geothermal reservoirs.

54

# Report 10

Equilibrium temperature evaluation of the thermal reservoirs in Yemen has been performed using different liquid phase geothermometers, such as SiO<sub>2</sub>, K<sub>2</sub>/Mg and Na/K. Silica temperatures range between 70 and 140°C, the highest values being calculated in the Mosh Al-Kafer area. The other geothermometers display very variable values. This is particularly true for the Na/K temperatures, these values being strongly affected by mixing processes with seawater or connate waters, jeopardizing the reliability of the geothermometers (Vaselli et al., 2001).

# 3. THERMAL ACTIVITY IN THE AL-LISI – ISBIL VOLCANIC AREA

# 3.1 Topography

In view of its topographical structure, the Republic of Yemen is divided into four regions (Figure 2):

*Region I - Tihama plain*: This area includes the coastal plains overlooking the Red Sea, the Gulf of Aden and the Arabian Sea. They are connected to each other forming a coastal strip that extends for 2400 km. The width of the plains ranges from 30 to 60 km.

*Region II - Highlands and high plateau*: This represents a large area of the country. It stretches longitudinally from the north to the south and transversally from the west to the east, resembling the letter "*L*". These heights descend in different directions. There are a number of basins, of considerable agricultural importance, such as the Jahran flatland in the Dhamar area. The elevation in this region is in the range 1000-3666 m; the mountain peaks include Isbil and Al-Lisi (Figure 3).

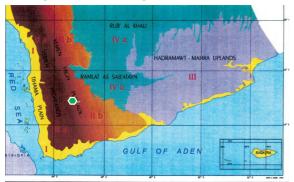




FIGURE 2: Topographical map of Yemen with a hexagon marking the study area

FIGURE 3: Al-Lisi volcanic mountain

In general, the climate varies but we can say that there are two long seasons: summer and winter. In the *mountainous* areas, the weather is moderate in summer and cold in winter during the night and in the early morning. The average temperature ranges from 10 to 19°C in summer, and from 8 to -1°C in winter. Rainfall is controlled by the monsoon, and it is estimated that the annual rainfall ranges between 400 and 500 mm, concentrated especially in July and August but also in March and April.

According to Van der Gun and Ahmed (1995), the annual rainfall is 338 mm with an average temperature of 16°C. Natural springs of both thermal and cold groundwater are not encountered. Resistivity *soundings* at the foot of Jabal Isbil indicate groundwater potential at depths greater than 200 m b.gl. (Sporry, 1991). Similarly, water wells in the Al-Lisi area supply water from >200 m depth. Groundwater is not overabundant in the Dhamar-Rada'a area. Discharge for irrigation has led to local significant declines of groundwater levels (Van der Gun and Ahmed, 1995). According to water balance calculations for the Qa'Shirah catchment area (several km southwest of Al-Lisi), only 4% of the precipitation reaches groundwater for recharge, corresponding to 13 mm/a (Klaffke, 1987). However, this recharge contributes mainly to the shallow aquifer which may have developed in the tertiary volcanic rocks. Quaternary and tertiary volcanic rocks consist of alternating layers with more or less permeable material (Wagner et al., 2007).

#### Al-Kohlani

56

*Region III - Hadramawt – Mahra uplands:* This area lies to the east and south of the heights going in parallel to the heights towards the Empty Quarter. The maximum elevation of this area is 1500 m in the western part and 1000 m in the eastern part.

*Region IV - The Empty quarter (Alrub AlKhali) and Ramlat As Sab'atayn*: This is a Yemeni desert area located to the north of the Hadhramout highlands, and to the south of the western heights. This area consists of desert plains covered with gravel, sand and sandy dunes.

*The islands*: *There* are 120 islands, most of which are located in the Red Sea. The biggest islands are Kamaran, Greater Hunaish, Minor Hunaish, Zaqar, Zubair, Al-Tayr and the strategic island of Meon at the Bab Al-Mandeb. In addition there are islands located in the Gulf of Aden and the Arabian Sea, the largest of which is Soqutra.

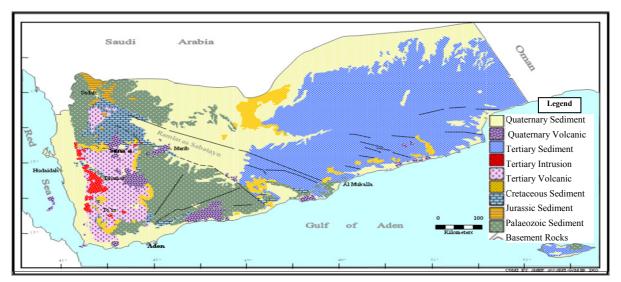


FIGURE 4: Geological map of Yemen

#### 3.2 Geology and tectonics

The young volcanic series of Yemen are of the age 10-5 Ma (late Miocene to Recent) and they include eight volcanic fields with recent volcanic activities (Figure 4). One of them is the Dhamar-Rada'a

volcanic field (Figure 5) (extensive Quaternary volcanics) which covers an area of about 1477  $km^2$ . It is also characterized by both central and fissure activities and has been affected by intense vertical tectonism, resulting in the formation of horst and graben structural patterns. It is also characterized by volcanic cones, domes, sheets and lava flows. The field is mainly composed of basaltic lava flows, and lithified and stratified basic tuffs and agglomeratic pyroclastics. Less common are differentiated rock-types such as rhyolite of peralkaline character. The exception is the Al-Lisi volcano which consists entirely of acidic rocks such as rhyolite and obsidian lava flows, acidic tuffs and ash rings (Mattash et al., 2001).

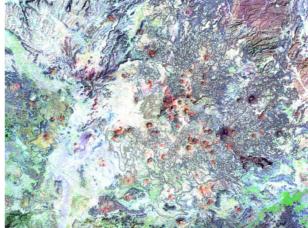


FIGURE 5: Landsat image, showing the Dhamar volcanic field; location is shown in Figure 1

### Report 10

Al-Lisi-Isbil geothermal field is situated in the centre of the Dhamar-Rada'a volcanic field 15 km east of Dhamar city, near the main road between Dhamar and Rada'a. The Al-Lisi volcano marks the western border of the rim; Jabal Isbil is located at the eastern rim. The latest stage of activity created the Al Lisi volcano and an explosive crater to the south. The Isbil stratovolcano developed in the eastern study area. Several Quaternary-recent volcanic cones, craters and collapsed caldera indicate hydrothermal activity (Mattash et al., 1998).

Two fumaroles have been found discharging from pyroclastic deposits, mainly of obsidian volcanic glass underlying the rhyolitic lava flows (Mattash et al., 2005). Recent fissure basaltic activity occurred throughout the whole area, mainly after the terminal effusive stages of the Al-Lisi and Hammam -Isbil volcanoes. They have E-W trending fractures, which served as feeding fissures for these basalts. A structural graben is associated with the Quaternary volcanic activity, hot springs discharging from the side of the valleys with fault direction NW-SE, parallel to the main Red Sea fault. Some faults were found with a NNE-SSW direction, and an E-W direction that is parallel to the main fault in the Gulf of Aden (Mattash and Al-Ganad, 2002).

The chronological sequence of lithological units is as follows:

| • | Holocene - Recent                 | Alluvial and wadi gravel         |
|---|-----------------------------------|----------------------------------|
| • | Pliocene to Holocene - Quaternary | Recent volcanics                 |
| • | Paleocene Tertiary volcanics      | Yemen Trap series (YTS)          |
| • | Mesozoic - Cretaceous             | Tawilah sandstone formation      |
| • | Precambrian                       | Basement, undifferentiated rocks |

*Basement, undifferentiated rocks:* The Precambrian rocks (low- to medium-metamorphic rocks) consist of meta-sediments (sericite-chlorite schist) and meta-volcanic rocks (gneisses), with marked foliation that outcrop to the north and east of Dhamar city. The basement is unconformably overlain either by the Tawilah sandstone formation or the volcanic Trap series.

*Tawilah sandstone formation (Cretaceous):* The Tawilah formation consists of cross-bedded continental sandstone. It is overlain by the Isbil volcanics to the north of Dhamar city which is unconformably underlain by the Precambrian gneiss. The sandstone beds have thicknesses up to 200 m north of Dhamar and 30 m near Isbil east of Dhamar, but up to 1200 m to the west of Dhamar, dipping to the west. The sandstone varies from typical sandstone to pebbles (Al-Kubati, 2005).

*Tertiary volcanics, Yemen Trap series (YTS):* Tertiary volcanics lie directly above the Tawilah formation and consist of ash, tuff and ignimbrite, interbedded with extensive basaltic lava flows. In some areas of Yemen, the thickness of the YTS reaches up to 2000 m; but around the area of Dhamar to Rada'a, the thickness ranges from 900 to 1000 m. These volcanic layers formed an extension plateau at the end of the Tertiary period cut by numerous vertical faults.

*Recent volcanics – Quaternary:* The Quaternary volcanics are represented by central and fissure volcanism. The fissure volcanism is characterized by widespread basaltic lava flows and spatter cones, extensive basaltic obsidians, and pumices in the Dhamar-Rada'a area. Al-Lisi and Isbil comprise the two large volcanic systems in the area (Volcanic complex) (Figures 6 and 7).

The Al-Lisi volcanic area has the following features:

- Phreatic explosion crater, south of Al-Lisi, the rim is 10 m high;
- Al-Lisi volcano with rhyolithic lava flows, explosive activity, 330 m pyroclastic cone, surge and fall deposits, obsidian lava flow (Chiesa et al., 1983);
- Ash rings 15 km<sup>2</sup> pyroclastic deposits, pumice and obsidian lithics;
- Lava domes rhyolithic, peralkaline obsidian, up to 150 m high.

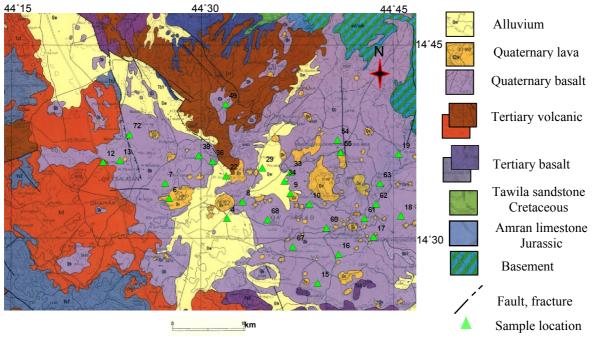


FIGURE 6: Geological map of the study area

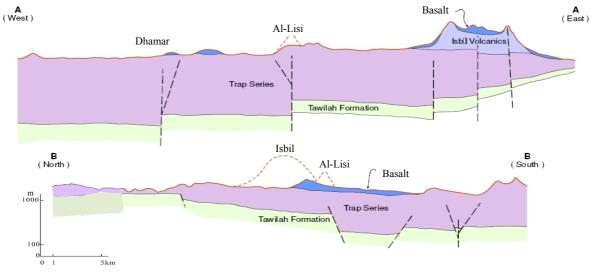


FIGURE 7: Geological cross-sections through the Al-Lisi – Isbil volcanic field (Wagner et al., 2007; Al-Kubati, 2005; from ELC, 1981)

The Isbil volcanic complex has the following features:

- Post-caldera silicic activity, related to NNW-SSE trending fissures, 10 m surge deposits, 20 m fall deposits;
- Caldera collapse in the east part of Isbil volcano;
- Pumice fall, 25 m thick, and pyroclastic flows;
- Isbil volcano lava flows (3-15 m thick) with minor ignimbritic and pyroclastic deposits.
- Trachytic to rhyolitic composition, overlying Dhamar ignimbrites (Wagner et al., 2007).

58

#### 3.3 Geophysical studies

In July 2007 a geophysical survey was carried out by a geophysical survey team of GSMRB with German cooperation. Five vertical electrical soundings (VES) were carried out using the Schlumberger configuration with a half current spread line (AB/2) of 2000 m, to study the vertical boundaries of the aquifer system. Four of these sites were selected by the German experts and the

fifth one was executed beside a drilled well which is sealed by cement as a result of emissions of high temperature steam during drilling.

The field data were acquired by the resistivity equipment: SYSCAL R2, an automatic direct current resistivity meter, with a maximum power output of 250 Watt. The results of the geo-electrical study in Al-Lisi area are presented in a geo-electrical crosssection in a W-E profile from sounding VES 2 to VES 4 (Figure 8). The profile has a total length of 11 km connecting 5 VES's. The cross-section illustrates the hydrogeological setting of the area.

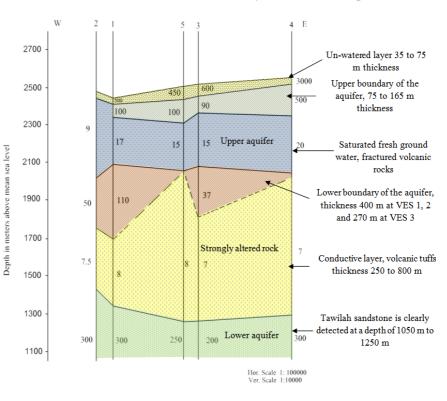


FIGURE 8: Geo-electrical cross-section with VES number and resistivity reading (mod. after Al Shehari and Al Hammadi, 2007)

The study found the existence of a conductive layer directly under the fresh water aquifer in VES 4 & 5 while they are separated by a permeable layer at VES 1, 2 & 3. This may explain the increase in water temperature of the groundwater in some places, where recent studies show that the conductive layer is strongly altered rock and the geothermal layer is comprised of Tawilah sandstone. It is recommended that an exploratory borehole be drilled to a depth of 1250 m at location VES 3 to confirm the geo-electrical model and to study the geothermal aquifer.

#### 4. CHARACTERISTICS OF THERMAL FLUIDS

The composition of thermal fluids depends on many factors. The most important are temperature dependent reactions between host rock and fluid. Leaching also plays an important role when the amount of a particular constituent is too small to achieve equilibrium. At the same time, mixing, boiling and cooling may have considerable influence on the final composition of thermal fluids.

The wells in the Al-Lisi – Isbil area were sampled for chemical analysis for the following elements and compounds; Ca, Mg, Na, K, HCO<sub>3</sub>, SO<sub>4</sub>, Cl, NO<sub>3</sub>, B, SiO<sub>2</sub>, F, Br, Li, and total dissolved solids (TDS) while NH<sub>4</sub>, pH, conductivity and temperature were measured in the field. Field work was carried out by an Italian and Yemeni team in 2007 with the main focus on the north to east Dhamar province, in particular the Al-Lisi – Isbil area, after previous work and investigations had established a

considerable geothermal potential in western Yemen. The samples were analyzed at the laboratories of the Department of Earth Sciences at the University of Florence, Italy, and the CNR – Institute of Geosciences and Earth Resources in Florence.

All the solutes were determined with standard procedures using AAS (Analyst 100 Perkin Elmer), Ion Chromatography (Dionex 100) and Colorimetry (Philips Unicam). Water sample were collected from hot and cold wells as follows:

- 1. 125 ml in a plastic bottle for the determination of anions and B; and
- 2. 50 ml in a plastic bottle for the determination of cations, acidified with 0.25 ml of concentrated and purified HNO<sub>3</sub>.

Results of chemical analysis for the samples from the 29 wells are listed in Table 1. The data were plotted in different triangular classification diagrams, mixing model diagrams, etc. The data were run by the WATCH program for speciation and the calculation of mineral equilibrium. Eight samples were selected for the plotting of mineral saturation log (Q/K) diagrams. The relationship between chloride content and other components was investigated.

| TABLE 1: Chemical composition of geothermal waters from Al-Lisi – Isbil area in Yemen |
|---|
| (concentration in mg/kg)  |

|         |                   |           |          |       |        |      |      |       | -    | 111 1 | 0    | - 0) |      |                  |        |     |                 |        |      |         |      |      |        |
|---------|-------------------|-----------|----------|-------|--------|------|------|-------|------|-------|------|------|------|------------------|--------|-----|-----------------|--------|------|---------|------|------|--------|
| Samples | Name of wells     | Longitude | Latitude | elev. | depth  | T°C  | pН   | cond. | TDS  | Ca    | Mg   | Na   | Κ    | HCO <sub>3</sub> | $SO_4$ | Cl  | $\mathrm{NH}_4$ | $NO_3$ | В    | $SiO_2$ | F    | Br   | Li     |
| 4       | Al Lisi well      | 44 31 58  | 14 31 33 | 2460  | 150.00 | 29.0 | 7.01 | 1116  | 593  | 31.0  | 13.0 | 118  | 3.7  | 417              | 2      | 9   | 0.04            | 0.95   | 0.48 | 35.0    | 0.56 | 0.02 | 0.46   |
| 6       | Jabel Al Dar      | 44 27 23  | 14 33 06 | 2415  | 350.00 | 45.0 | 7.00 | 1267  | 874  | 25.0  | 7.5  | 212  | 4.4  | 616              | 6      | 3   | 0.06            | 0.03   | 0.06 | 27.0    | 0.12 | 0.02 | 0.14   |
| 7       | Beer Gra'yah      | 44 27 04  | 14 34 17 | 2407  | 120.00 | 30.0 | 7.94 | 593   | 400  | 9.0   | 9.0  | 91   | 3.9  | 282              | 3      | 2   | <0,01           | 0.04   | 0.31 | 15.0    | 0.10 | 0.03 | 0.02   |
| 8       | Al Makhafish      | 44 33 11  | 14 32 51 | 2470  | 160.00 | 33.0 | 7.18 | 963   | 550  | 40.0  | 15.0 | 91   | 5.1  | 390              | 3      | 6   | <0,01           | 0.87   | 0.59 | 30.0    | 0.24 | 0.04 | 0.27   |
| 9       | Al Ku'aa          | 44 36 58  | 14 33 29 | 2525  | 240.00 | 36.0 | 6.99 | 733   | 519  | 51.0  | 25.0 | 48   | 8.2  | 384              | 1      | 2   | <0,01           | 1.67   | 2.10 | 33.0    | 0.14 | 0.01 | 0.04   |
| 10      | Isbil well        | 44 38 28  | 14 32 39 | 2535  | 180.00 | 38.0 | 7.05 | 633   | 410  | 38.0  | 19.0 | 40   | 8.9  | 301              | 1      | 2   | <0,01           | 1.59   | 0.36 | 35.0    | 0.15 | 0.01 | 0.03   |
| 12      | Al-Wesabi Factory | 44 22 10  | 14 35 55 | 2420  | 180.00 | 28.0 | 8.05 | 511   | 301  | 34.0  | 9.0  | 34   | 2.6  | 212              | 3      | 6   | <0,01           | 2.82   | 0.06 | 9.0     | 0.05 | 0.03 | 0.01   |
| 13      | Al Meshooaf       | 44 23 29  | 14 36 02 | 2420  | 200.00 | 43.0 | 7.83 | 344   | 170  | 19.0  | 3.5  | 21   | 2.1  | 121              | 1      | 2   | 0.02            | 1.28   | 0.22 | 10.0    | 0.05 | 0.01 | < 0.01 |
| 15      | Sanaban           | 44 39 07  | 14 26 30 | 2372  | 240.00 | 35.0 | 7.80 | 427   | 304  | 7.5   | 4.2  | 71   | 1.7  | 215              | 2      | 3   | <0,01           | 0.11   | 0.06 | 11.0    | 0.45 | 0.03 | < 0.01 |
| 16      | Gomol             | 44 40 47  | 14 28 45 | 2417  | 150.00 | 29.0 | 6.55 | 1412  | 731  | 57.0  | 19.0 | 115  | 9.0  | 515              | 2      | 14  | <0,01           | 0.91   | 1.70 | 42.0    | 0.18 | 0.04 | 0.25   |
| 17      | Sainm             | 44 43 33  | 14 30 06 | 2407  | 280.00 | 37.0 | 7.64 | 700   | 333  | 17.0  | 9.0  | 61   | 5.5  | 232              | 2      | 6   | <0,01           | 1.29   | 3.70 | 36.0    | 0.21 | 0.02 | 0.04   |
| 18      | Al Haemedy        | 44 45 43  | 14 31 45 | 2378  | 215.00 | 38.0 | 7.02 | 660   | 691  | 33.0  | 22.0 | 121  | 15.0 | 495              | 2      | 3   | <0,01           | 0.77   | 1.40 | 13.0    | 0.31 | 0.02 | 0.34   |
| 19      | Al Abal           | 44 45 32  | 14 36 32 | 2280  | 170.00 | 28.0 | 7.49 | 586   | 361  | 31.0  | 13.0 | 47   | 3.1  | 263              | 2      | 2   | <0,01           | 2.21   | 4.80 | 18.0    | 0.19 | 0.02 | 0.02   |
| 22      | Al Mufajara       | 44 31 54  | 14 34 51 | 2410  | 146.00 | 33.0 | 7.09 | 367   | 268  | 34.0  | 6.5  | 28   | 2.0  | 181              | 9      | 7   | 0.02            | 5.02   | 0.87 | 28.0    | 1.06 | 0.08 | 0.01   |
| 29      | Mufaid            | 44 34 45  | 14 35 28 | 2563  | 180.00 | 40.0 | 7.25 | 386   | 215  | 27.0  | 6.0  | 22   | 3.6  | 152              | 2      | 2   | 0.06            | 3.80   | 0.46 | 36.5    | 0.14 | 0.04 | 0.01   |
| 33      | Beer Mudafer      | 44 36 59  | 14 35 08 | 2574  | 210.00 | 42.0 | 7.29 | 586   | 473  | 52.0  | 15.0 | 54   | 8.4  | 303              | 20     | 21  | <0,01           | 25.00  | 0.17 | 39.2    | 1.30 | 0.17 | 0.02   |
| 34      | Garbat Almarbou   | 44 36 31  | 14 34 26 | 2559  | 230.00 | 43.0 | 7.58 | 510   | 368  | 40.0  | 12.0 | 41   | 8.3  | 229              | 19     | 19  | <0,01           | 22.00  | 0.34 | 45.2    | 1.14 | 0.16 | 0.02   |
| 36      | Qafa Aldymah      | 44 30 49  | 14 35 58 | 2449  |        | 31.0 | 6.32 | 365   | 266  | 30.0  | 9.5  | 29   | 1.7  | 168              | 13     | 15  | 0.03            | 20.00  | 0.34 | 29.0    | 3.20 | 0.14 | 0.05   |
| 38      | Qsm Alwatham      | 44 29 44  | 14 36 26 | 2434  | 270.00 | 35.0 | 6.86 | 371   | 275  | 33.0  | 8.2  | 25   | 5.0  | 152              | 37     | 15  | <0,01           | 0.98   | 0.11 | 44.2    | 1.80 | 0.15 | 0.02   |
| 49      | Bani Rakapan      | 44 31 51  | 14 40 24 | 2505  | 192.00 | 41.0 | 9.07 | 325   | 214  | 2.7   | 0.03 | 62   | 1.8  | 107              | 22     | 18  | <0,01           | 17.00  | 0.76 | 17.5    | 0.32 | 0.31 | < 0.01 |
| 54      | El Wathah         | 44 40 42  | 14 37 38 | 2485  | 140.00 | 32.5 | 7.77 | 405   | 268  | 26.0  | 7.2  | 34   | 6.5  | 157              | 20     | 17  | <0,01           | 21.00  | 1.01 | 25.5    | 1.80 | 0.21 | 0.01   |
| 55      | El Najd           | 44 40 56  | 14 36 40 | 2525  | 240.00 | 39.0 | 7.77 | 471   | 299  | 21.0  | 10.0 | 59   | 6.4  | 160              | 25     | 18  | <0,01           | 39.00  | 0.60 | 18.8    | 3.40 | 0.24 | 0.02   |
| 61      | El Bakalah        | 44 42 50  | 14 31 32 | 2500  | 320.00 | 38.5 | 7.91 | 617   | 414  | 21.0  | 7.6  | 96   | 8.8  | 203              | 26     | 52  | <0,01           | 22.00  | 1.30 | 32.0    | 4.10 | 0.28 | 0.06   |
| 62      | El Homaida        | 44 43 45  | 14 32 39 | 2430  | 300.00 | 56.0 | 7.16 | 666   | 513  | 27.0  | 5.5  | 110  | 13.0 | 295              | 28     | 34  | 0.13            | 14.00  | 1.20 | 49.3    | 5.70 | 0.20 | 0.09   |
| 63      | El Uglah          | 44 44 03  | 14 34 15 | 2370  | 234.00 | 59.0 | 6.48 | 2120  | 1809 | 102.0 | 35.0 | 352  | 46.0 | 1019             | 124    | 131 | 0.26            | 9.80   | 5.70 | 25.0    | 2.30 | 0.63 | 0.88   |
| 67      | El Harug          | 44 37 11  | 14 29 20 | 2420  | 130.00 | 30.0 | 6.50 | 1760  | 1202 | 90.0  | 29.0 | 252  | 12.0 | 475              | 30     | 314 | 0.03            | 11.00  | 6.50 | 24.0    | 3.30 | 0.96 | 0.55   |
| 68      | El Duhaimi        | 44 35 10  | 14 31 27 | 2490  |        | 34.5 | 6.50 | 1986  | 1316 | 67.0  | 21.0 | 330  | 21.0 | 476              | 53     | 348 | 0.01            | 12.00  | 7.70 | 19.8    | 4.50 | 1.20 | 0.68   |
| 69      | El Atheel         | 44 39 50  | 14 30 49 | 2465  | 200.00 | 36.5 | 6.65 | 1885  | 968  | 121.0 | 39.0 | 112  | 17.0 | 426              | 48     | 205 | <0,01           | 15.00  | 2.20 | 31.5    | 0.91 | 0.76 | 0.09   |
| 72      | Taher             | 44 24 15  | 14 38 03 | 2315  | 150.00 | 21.0 | 7.28 | 923   | 438  | 72.0  | 14.0 | 30   | 2.4  | 268              | 32     | 20  | 0.03            | 11.00  | 0.68 | 8.5     | 0.22 | 0.24 | < 0.01 |

### 4.1 Classification of thermal waters

*The Cl-SO*<sub>4</sub>-*HCO*<sub>3</sub> *triangular diagram:* Most geochemical techniques may with confidence be applied to specific types of fluids with limited ranges of composition. For instance, most ionic solute geothermometers work only if they apply to neutral waters containing chloride as the major ion. Any such interpretation of geothermal water samples, therefore, is best carried out on the basis of an initial classification, for example in terms of their major anions Cl<sup>-</sup>, SO<sub>4</sub><sup>-2</sup> and HCO<sub>3</sub><sup>-</sup> (Giggenbach, 1991). These triangular diagrams are used for the classification of natural waters and for the classification of geothermal water on the basis of major anion concentrations. It helps to separate immature unstable

Al-Kohlani

waters, mature waters, peripheral waters, steam-heated waters and volcanic waters. Moreover it may give an indication of mixing relationships or geographic groupings.

Chloride is used as a tracer in geothermal investigations because it is a conservative ion in geothermal fluids, as it does not take part in reactions with rocks after it has dissolved. Chloride does not precipitate after it has dissolved; it does not return to the rock so its concentration is independent of the mineral equilibria that control the concentration of the rock-forming constituents. The position of a data point on such a triangular plot is obtained first by a summation of concentrations, Ci (mg/l), of all three constituents involved:

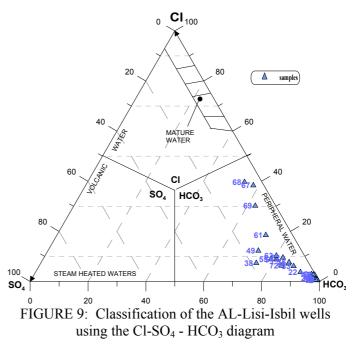
$$S = C_{Cl} + C_{SO4} + C_{HCO3}$$
(1)

The next step is to obtain the percent (%) of every constituent using the following equations:

% 
$$Cl = 100 C_{Cl}/S$$
  
%  $SO_4 = 100 C_{SO4}/S$  (2)  
%  $HCO_3 = 100 C_{HCO3}/S$ 

The results of calculations for samples collected from the Al-Lisi – Isbil area are shown in Figure 9. Most of the samples are located in the high bicarbonate region in or near to the HCO<sub>3</sub> corner. Thus, they can be classified as peripheral waters that may have mixed with cold groundwater or  $CO_2$  from a magmatic source. Only three samples were located a bit closer to the chloride region of the diagram but are still within the bicarbonate water region which suggests some degree of mixing with cold water.

*The B-Cl-Li triangular diagram:* The B content of thermal fluids is likely to reflect to some degree the maturity of a geothermal system; because of its volatility it is expelled during the early heating up stages. In such a case, fluids from older hydrothermal systems can be



expected to be depleted in B (also As, Sb and Hg) as opposed to younger hydrothermal systems. In geothermal systems Li is used as a tracer, because it is the alkali metal least affected by secondary processes for initial deep rock dissolution and as a reference for evaluating the possible origin of two important conservative constituents of geothermal waters, Cl and B. Once added, Li remains largely in solution. It is, however, striking that both Cl and B are added to the Li containing solutions in proportions close to those in crustal rocks. At higher temperatures Cl occurs as HCl and B as H<sub>3</sub>BO<sub>3</sub>. Both are volatile and able to be mobilized by high temperature steam. They are, therefore, quite likely to have been introduced with the magmatic vapour invoked above to lead to the formation of deep acid brine responsible for rock dissolution. At low temperatures the acidity of HCl increases rapidly, and is soon converted by the rock to the less volatile NaCl. B remains in volatile form to be carried in the vapour phase even at lower temperatures. The B/Cl ratio is often used to indicate a common reservoir source for the waters. Care must be taken in applying such interpretation since waters from the same reservoir may show differences in this ratio, due to changes in lithology at depth over a field (example, the occurrence of a sedimentary horizon), or by the absorption of B into clays during lateral flow (Giggenbach, 1991).

The position of a data point in such a triangular plot is simply obtained by first obtaining the sum S of the concentrations, Ci (in mg/l), of all three constituents involved: S

$$= C_{Cl}/100 + C_{Li} + C_B/4 \tag{3}$$

The next step consists of the evaluation of "% -*Cl*", "% -*Li*" and "% -*B*/4" according to:

$$"0% - Cl" = 100 C_{Cl}/100/S = C_{Cl}/S 
 "0% - Li" = 100 C_{Li}/S 
 "0% - B/4" = 100 C_B/4/S
 (4)$$

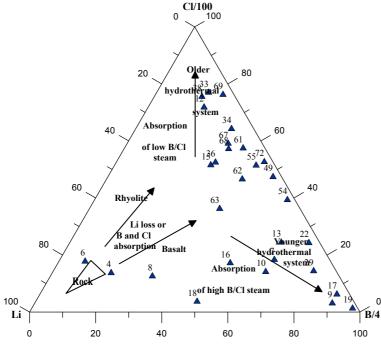


Figure 10 shows that most of the samples plot near the B - Cl line which may indicate that the fluid migrates from the young hydrothermal system where the high absorption of B/Cl steam from degassing fresh magma, towards the old hydrothermal system area where there is low absorption of B/Cl steam.

*Na-K-Mg triangular diagram:* The Na-K-Mg diagram was constructed by Giggenbach (1988). It is essentially based on the temperature dependence of the two reactions:

FIGURE 10: Classification of the Al-Lisi – Isbil thermal fluids using the B-Cl-Li diagram

$$K-feldspar + Na^{+} = Na-feldspar + K^{+}$$
(5)

$$0.8 \text{ K-mica} + 0.2 \text{ chlorite} + 5.4 \text{ silica} + 2 \text{ K}^{+} = 2.8 \text{ K-feldspar} + 1.6 H_2O + Mg^{+2}$$
(6)

The diagram is used to evaluate equilibrium conditions between the geothermal water and reservoir rocks. The main advantage of this diagram is its ability to picture the position of a large number of samples simultaneously, permitting delineation of mixing trends and groupings. It separates well the position of waters resulting from the two end member processes, rock dissolution and equilibration. As in the other triangular diagrams, the sum is calculated to evaluate "-Na" and "-Mg", where  $C_i$ is in mg/l. Na, K and Mg concentrations of waters in equilibrium with this assemblage are accessible to rigorous evaluation. The coordinates of a point on the diagram are calculated by:

$$S = C_{Na} / 1000 + C_K / 100 + \sqrt{C_{Mg}}$$
<sup>(7)</sup>

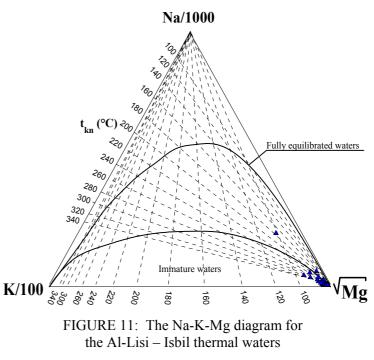
$$\%Na = C_{Na}/10 S$$
  

$$\%K = C_K/S$$
  

$$\%Mg = \sqrt{C_{Mg}}/S$$
(8)

The area of partial equilibrium suggests either a mineral that has dissolved but not attained equilibrium, or a water mixture that has reached equilibrium (e.g. geothermal water) mixed with dilute unequilibrated water (e.g. cold groundwater). Points close to the  $\sqrt{Mg}$  corner usually suggest a high proportion of relatively cold groundwater, not necessarily "immature".

Figure 11 shows that almost all the samples are located in the area of immature waters, very close to the Mg corner of the diagram. This could mean they have a high proportion of cold groundwater, i.e. the thermal fluids are a mixture of cold groundwater, and they have not attained equilibrium. The relatively high Mg concentration is due to the bicarbonate type of the water. Therefore, it is difficult if not unsuitable to estimate reservoir temperature. One sample plotted



between partial equilibrium and fully equilibrated water.

# 4.2 Geothermometers

The application of chemical geothermometers is one of the most important methods for the exploration and development of geothermal resources. It is useful for predicting subsurface or reservoir temperatures and obtaining valuable information about what is happening in the reservoir during exploration. Cooling of the water in the upflow zones of a geothermal system may occur by conduction, boiling and/or mixing with cold water. The basic assumption is that a temperaturedependent equilibrium is attained between the fluid and the minerals in the reservoir. The temperatures in geothermal reservoirs are generally not homogeneous, but variable, both horizontally and vertically, so geothermometry is useful for revealing the temperature of the aquifer feeding the drillholes. Temperatures encountered in a deep drillhole may be higher than those indicated by chemical geothermometry, particularly if the waters investigated are fed by shallow aquifers (Arnórsson, 1991). The silica (quartz and chalcedony), Na/K and Na-K-Ca geothermometers are the most important.

63

*Silica geothermometers:* The dissolved concentration of silica in a hydrothermal solution can generally be used as one of the more reliable chemical geothermometers. The solubility reactions for silica minerals are invariably expressed as:

$$SiO_2(s) + 2 H_2O = H_4SiO_4(aq)$$
(mineral)
(silicic acid)
(9)

The silica temperature is based on the equilibrium between quartz or chalcedony and the unionized silica in a thermal fluid. Experiences show that chalcedony temperature is commonly more realistic in low-temperature waters than quartz temperature (Arnórsson, 1975). Both quartz and chalcedony geothermometers were used to estimate subsurface temperatures in the present study. But there are various silica minerals with different solubilities, and it should be known which silica mineral is controlling the dissolved silica concentration when using the silica geothermometers. It means that different silica geothermometers are valid at different temperatures. Also, in mature sedimentary rocks which contain less reactive minerals, despite being a low-temperature field with temperatures

less than 100°C, quartz can control dissolved silica. In another situation, chalcedony may control dissolved silica up to temperatures as high as 180°C, maybe because chalcedony is probably not a separate mineral but a mixture of fine-grained quartz and moganite which, with time, probably all changes to quartz (Gíslason et al., 1997). Therefore, there is ambiguity in the use of silica geothermometers at temperatures less than about 180°C. In general, the quartz geothermometer works well in high-temperature reservoirs, but the chalcedony geothermometer is better for low-temperature reservoirs. The reason is that, at low temperatures, the rate of quartz precipitation does not cope with the rate of silica release into solution by dissolving primary minerals; on the other hand, chalcedony is unstable at temperatures above 120-180°C. The quartz geothermometer may be applicable down to 100°C in old systems, but in young systems, it may not be applicable below 180°C. The following equations for silica geothermometers have been proposed:

Quartz - no steam loss (Fournier, 1977):

$$t^{\circ}C = \frac{1309}{5.19 - \log SiO_2} - 273.15$$
(10)

Quartz – maximum steam loss at 100°C (Fournier, 1977):

$$t^{\circ}C = \frac{1522}{5.75 - \log SiO_2} - 273.15$$
(11)

Chalcedony - no steam loss (Fournier, 1977):

$$t^{\circ}C = \frac{1032}{4.69 - \log SiO_2} - 273.15$$
(12)

Chalcedony – maximum steam loss at 100°C (Fournier, 1977):

$$t^{\circ}C = \frac{118}{5.09 \cdot \log SiO_2} - 273.15$$
(13)

Chalcedony - no steam loss (Arnórsson et al., 1983):

$$t^{\circ}C = \frac{1112}{4.91 - \log SiO_2} - 273.15$$
(14)

Chalcedony – maximum steam loss at 100°C (Arnórsson et al., 1983):

$$t^{\circ}C = \frac{1264}{5.31 - \log SiO_2} - 273.15$$
(15)

*Cation geothermometers:* Cation geothermometers are based on ion exchange reactions with temperature-dependent equilibrium constants. A typical example is the exchange of Na+ and K+ between co-existing alkali feldspars:

$$NaAlSi_{3}O_{8} + K^{+} = KAlSI_{3}O_{8} + Na^{+}$$
(16)  
(albite) (orthoclase)

Two assumptions are made, that the activities of the solid reactions are unity and the activities of the solid reactions of the dissolved species are equal to their molal concentrations in aqueous solution. The equilibrium constant, *Keq* for this reaction is:

$$Keq = \frac{(KAlSi_{3}O_{8})(Na^{+})}{(NaAlSi_{3}O_{8})(K^{+})}$$
(17)

If the activities of the solid reactants are assumed to be unity and the activity of the dissolved species is about equal to their molal concentrations, the equation will be reduced to:

$$Keq = \frac{(Na^+)}{(K^+)}$$
(18)

Several authors have suggested empirical Na/K geothermometers based on experiments and obtained different results due to work with different minerals. Basaltic minerals usually give low values (Arnórsson et al., 1983) but andesitic ones high values (Giggenbach, 1988) at low temperatures. At high temperatures they converge and give similar values. The Na/K ratio works generally well for estimating temperatures of water above 200°C.

The following formulae, based on empirical correlations presented by Arnórsson et al. (1983) and Giggenbach (1988), are used in this report; the concentrations of Na and K are in mg/kg:

Na-K temperature (Arnórsson et al., 1983):

$$t^{\circ}C = \frac{933}{0.993 - \log(\text{Na/K})} - 273.15$$
(19)

Na-K temperature (Giggenbach, 1988):

$$t^{\circ}C = \frac{1390}{1.75 - \log(\text{Na/K})} - 273.15$$
(20)

*K-Mg geothermometer:* The K-Mg geothermometer is based on the equilibrium between water and the mineral assemblage K- feldspar, K- mica and chlorite (Giggenbach, 1988). It has been observed that it responds fast to changes in the physical environment and, thus, usually gives a relatively low temperature in mixed and cooled waters as compared to other geothermometers (concentrations are in mg/kg):

$$t^{\circ}C = \frac{4410}{14.4 - \log(K^2/Mg)} - 273.15$$
(21)

*Na-K-Ca geothermometer:* The Na-K-Ca geothermometer was developed by Fournier and Truesdell (1973) for application to waters with elevated  $Ca^{2+}$  contents that give anomalously high calculated temperature for the Na/K geothermometer. The relationships of Na<sup>+</sup>, K<sup>+</sup> and Ca<sup>2+</sup> were explained in terms of Ca<sup>2+</sup> participating in aluminium silicate reactions. The amounts of dissolved Na and K are therefore influenced by the dissolved Ca, even though the final amount of aqueous Ca may be controlled largely by carbonate solubility and carbon dioxide (Nicholson, 1993). The geothermometer is entirely empirical and assumes one type of base exchange reaction at temperatures above about 100°C (concentrations are in mg/kg):

$$t^{\circ}C = \frac{1647}{\log(\text{Na/K}) + \beta\{\log(\sqrt{\text{Ca/Na}}) + 2.06\} + 2.47} - 273.15$$
(22)

where  $\beta = 4/3$  for  $Ca^{1/2}/Na > 1$  and  $t < 100^{\circ}C$ ;  $\beta = 1/3$  for  $Ca^{1/2}/Na < 1$  or if  $t > 100^{\circ}C$ .

The results of calculated geothermometers for the waters from the wells in the Al-Lisi – Isbil area are listed in Table 2. The following can be seen:

- The K-Mg geothermometer shows values close to the measured ones.
- The silica chalcedony geothermometer gives similar values in some cases, but considerably higher in others, and lower in seven cases. It is considered likely that the chalcedony geothermometer gives a minimum value for the reservoir temperatures.

- The quartz geothermometer gives considerably higher values than the chalcedony and K-Mg geothermometers show, in nearly all cases.
- The Na-K geothermometers indicate higher temperatures but one cannot rely on the results due to reservoir mixing with cold waters, which makes these geothermometers unreliable.
- Disagreement between estimated temperatures of mentioned geothermometers might be due to mixing of samples with cold waters. Thus, there is no confidence to estimate the reservoir temperatures using these solute geothermometers.

| Well no. | T meas. | T quartz <sup>1</sup> | T chalcedony <sup>2</sup> | T Na-K <sup>3</sup> | T Na-K <sup>4</sup> | T K-Mg <sup>4</sup> |
|----------|---------|-----------------------|---------------------------|---------------------|---------------------|---------------------|
| 4        | 29      | 86                    | 55                        | 99                  | 154                 | 42                  |
| 6        | 45      | 75                    | 43                        | 75                  | 132                 | 51                  |
| 7        | 30      | 52                    | 20                        | 122                 | 173                 | 47                  |
| 8        | 33      | 80                    | 48                        | 145                 | 190                 | 47                  |
| 9        | 36      | 84                    | 52                        | 261                 | 279                 | 52                  |
| 10       | 38      | 86                    | 55                        | 289                 | 305                 | 56                  |
| 12       | 28      | 34                    | 3                         | 174                 | 212                 | 39                  |
| 13       | 43      | 37                    | 6                         | 202                 | 232                 | 44                  |
| 15       | 35      | 40                    | 9                         | 83                  | 139                 | 38                  |
| 16       | 29      | 94                    | 63                        | 176                 | 213                 | 57                  |
| 17       | 37      | 86                    | 55                        | 191                 | 224                 | 54                  |
| 18       | 38      | 47                    | 15                        | 225                 | 250                 | 66                  |
| 19       | 28      | 59                    | 27                        | 160                 | 201                 | 39                  |
| 22       | 33      | 76                    | 44                        | 167                 | 207                 | 37                  |
| 29       | 40      | 87                    | 56                        | 256                 | 275                 | 50                  |
| 33       | 42      | 90                    | 59                        | 250                 | 270                 | 58                  |
| 34       | 43      | 96                    | 65                        | 279                 | 296                 | 60                  |
| 36       | 31      | 78                    | 46                        | 148                 | 193                 | 31                  |
| 38       | 35      | 96                    | 65                        | 277                 | 294                 | 53                  |
| 49       | 41      | 47                    | 15                        | 94                  | 150                 | 95                  |
| 54       | 32      | 72                    | 40                        | 247                 | 290                 | 60                  |
| 55       | 39      | 60                    | 28                        | 211                 | 239                 | 56                  |
| 61       | 38      | 80                    | 49                        | 192                 | 225                 | 66                  |
| 62       | 56      | 100                   | 70                        | 220                 | 246                 | 79                  |
| 63       | 59      | 72                    | 40                        | 230                 | 255                 | 88                  |
| 67       | 30      | 70                    | 39                        | 130                 | 179                 | 58                  |
| 68       | 35      | 63                    | 31                        | 155                 | 199                 | 75                  |
| 69       | 37      | 81                    | 50                        | 247                 | 268                 | 63                  |
| 72       | 21      | 32                    | 1                         | 179                 | 215                 | 33                  |

| TABLE 2: Temperature of different geothermometers in °C |
|---|
| for the thermal waters in the Al-Lisi – Isbil wells     |

1) Fournier and Potter, 1982; 2) Fournier, 1977; 3) Arnórsson et al., 1983; 4) Giggenbach, 1988

# 4.3 Mineral-solution equilibria

The fundamental criterion for use of multiple mineral equilibria as chemical equilibrium in a thermodynamic system for estimating subsurface temperature is that, firstly, total Gibbs free energy is at a minimum. At constant temperature and pressure, the Gibbs free energy change in a chemical reaction is given by:

Report 10

Al-Kohlani

$$\Delta Gr = -RT lnK + RT lnQ = RT ln\left(\frac{Q}{K}\right)$$
(23)

where R = Gas constant;T = Temperature (K)

Secondly, the assumption has to be made that particular minerals attain equilibrium with the fluids in the reservoir because one of the thermodynamic properties of minerals and species is change with temperature and pressure. The effect of temperature is much greater than the effect of pressure in the temperature range from 0 to 350°C and pressure range from 1 to 200 bar, so that the effect of pressure on mineral-solution equilibrium can be neglected. Therefore, Reed and Spycher (1984) have suggested that the best estimate of reservoir temperature using geothermometers can be attained by simultaneously considering the state of equilibrium between specific water and many hydrothermal minerals as a function of temperature. In that case, if a group of minerals converge to equilibrium at a particular temperature, this temperature corresponds to the most likely reservoir temperature. The rising fluid through a body of rock has reacted chemically with the rock and, in the case with any chemical reaction, changes the system towards equilibrium. The choice of the minerals should include those known to occur as hydrothermal minerals in the area under study or in geothermal systems in general, but particularly those occurring in the same type of rock as the system under exploration. Minerals that should always be considered include quartz or chalcedony, the alkali feldspars (albite and microcline), calcite, in some cases anhydrite, fluorite and/or zeolites, smectite, chlorite, wairakite, prehnite, epidote and mica. For high-temperature geothermal systems pyrite, pyrrhotite and magnetite should also be considered.

The equilibrium state for a given reaction of a mineral and a solution in a geothermal system can be evaluated by the ratio of the equilibrium constant (K) for the given reaction to the reaction quotient (Q) (Arnórsson, 2000). The saturation indices (SI) for minerals in aqueous solutions at different temperatures were computed as:

$$SI = \log \frac{Q}{\kappa} = \log Q - \log K \tag{24}$$

where Q = Calculated ion activity product; K = Equilibrium constant.

The SI value for each mineral is a measure of the saturation state of the water phase with respect to the mineral phase. Values of SI greater than, equal to, and less than zero represent supersaturation, equilibrium and undersaturation, respectively, for the mineral phase with respect to the aqueous solution. If SI for calcite is higher than 0, the water can deposit calcite; if SI = 0 the solution is in equilibrium with calcite and will neither deposit nor dissolve calcite; and if SI is lower than 0, the water does not have a calcite deposition potential.

*Speciation and equilibrium - the WATCH program:* The computer programme WATCH (version 2.3) calculates the speciation of waters at a given temperature (Arnórsson et al., 1993; Bjarnason, 1994). It is quite useful for the interpretation of the chemical composition of geothermal fluids, as well as for non-thermal waters. Chemical analysis of samples collected at the surface can be used to compute the composition of aquifer fluids. The programme calculates aqueous speciation, using mass balance equations and chemical equilibrium. WATCH can also be used to calculate the composition of fluid for different designs of the geothermal plant. The WATCH program can also be used to compute the concentrations of the resulting species, activity products and solubility products when the equilibrated fluid is allowed to cool conductively or by adiabatic boiling from the reference temperature to some lower temperature. This is particularly useful in order to evaluate the scaling potential of the fluid. To evaluate the equilibrium minerals in the fluid, several runs of the WATCH programme were done for wells 49, 13, 54, 12, 15, 34, 38, 17 using the water sample analyses.

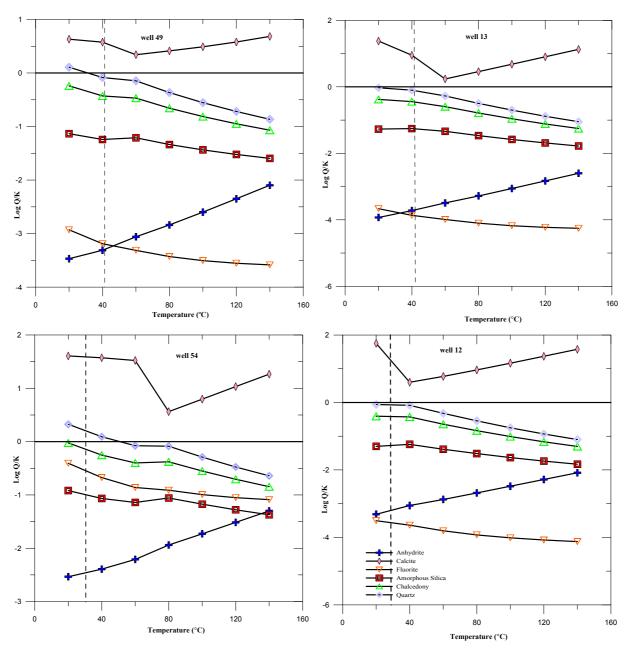


FIGURE 12: Saturation index (log Q/K) vs. temperature calculated with the WATCH program for wells in the Al-Lisi – Isbil field (Dhamar area)

Figure 12 shows saturation index (SI =  $\log Q/K$ ) diagrams for the temperature range 20-140°C calculated with the WATCH aqueous speciation program, which is useful for demonstrating reservoir temperatures. Results based on this method should be interpreted with caution as only three samples, from wells 34, 17 and 38, have acceptable ionic balances as calculated using the WATCH program and are slightly above 10%. The following results can be obtained from the diagrams:

- A similar pattern was found for most well samples and it does not show any conversion to the zero saturation indexes by any group of minerals. It means no clear temperature-rock equilibrium between all or most of the minerals and the thermal fluids can be found. This could be due to mixing or other processes such as the precipitation of some minerals.
- In almost all cases, lines for two minerals cross at a temperature below the saturation line and almost all minerals plot within the undersaturation zone, which may indicate more mixing with cold groundwater.

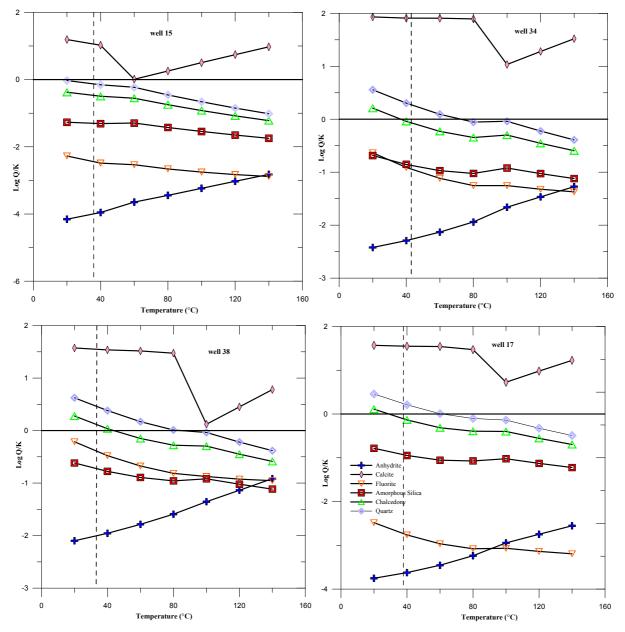


FIGURE 12 cont.: Saturation index (log Q/K) vs. temperature calculated with the WATCH programme for wells in the Al-Lisi – Isbil field (Dhamar area)

- The pattern of the calcite saturation index plots above the zero line (supersaturated zone) in all the diagrams and furthermore, calcite solubility is inversely related to water temperature.
- Unfortunately no analysis of (Al) was available which influences the results and restricts the number of possible minerals for calculating the saturation index.
- The saturation index (SI) can be applied for the evaluation of scaling potential of water. All minerals in the samples are undersaturated at the calculated temperature range, except calcite. As a result, the risk of precipitation of those minerals is low.

# 4.4 Mixing evaluations

*Evidence of mixing:* It is well known that the chemistry of geothermal water is characterized by equilibrium conditions between solutes and alteration minerals. It is also known that water formed by mixing geothermal water and cold groundwater or surface water may possess chemical characteristics

69

#### Al-Kohlani

too, so we can distinguish between mixed water from unmixed geothermal water. The hot rising water may show some evidence of the processes that can take place on its way to the surface, processes such as cooling by conduction, boiling or mixing with colder water, or maybe a combination of these processes. When this is the case, partial or complete chemical equilibration may or may not occur after mixing, and the chemical geothermometers indicate temperatures of the mixed water, not the hot water within the reservoir. The temperature of the hot water cannot be estimated from a solubility relationship unless mixing is taken into account.

Geothermal waters are often, but not always, much higher in dissolved solids than cold ground and surface waters. The main chemical characteristics of mixed water, which serve to distinguish them from equilibrated geothermal waters, include relatively high concentrations of silica in relation to the discharge temperature, low pH relative to the water salinity and high total carbonate, at least if the mixing has prevented boiling.

There are numerous methods that can be used to extract some evidence about the mixing of two waters such as the relationship between chloride, boron, silica, sulphate and mixing models. The linear or near-linear relationship between these parameters appears to be useful for evaluating mixing processes and indicate that mixing has occurred. A Schoeller diagram comprises the log concentrations of fluid components from a number of analyses and shows the effects of mixing. Mixing geothermal water with dilute water moves the line on the Schoeller vertically representing an analysis without changing its shape (Truesdell, 1991).

In this study there are some indications of mixing of different water types in the studied area, such as:

- There is a disagreement between the geothermometers. Silica geothermometer temperatures are lower than the Na-K temperatures.
- The mineral equilibria diagrams show no clear intersection to the zero saturation index by any group of minerals at a particular temperature.
- On the Giggenbach Cl-SO<sub>4</sub>-HCO<sub>3</sub> diagram, most of the samples plot in the area for mixed water.
- On the Giggenbach Na-K-Mg triangular diagram, all the samples plot in the partially equilibrated mixed water area.
- There is a nearly linear relationship between chloride and others constituents, suggested by Arnórsson (1985) to be a good indication of mixing.
- The Schoeller diagram for samples of thermal water from the study area indicates mixing.

Semi-linear relationships between Cl vs. B, Cl vs.  $SO_4$  and Cl vs. Na (Figure 13) are evidence which shows that ascending water might have been mixed with cold waters in the upflow zone as suggested by Arnórsson (1985). A few scattered samples do not concur and might be waters of different origin. The same semi-linear relationship can also be found for Cl vs.  $SiO_2$  although it is not as obvious. This is also an indication of mixing.

*Schoeller diagram:* The Schoeller diagram is used to classify the type of water. It may also be used to show changes over time for the different water types. The effect of mixing with dilute water is to move the line representing an analysis vertically without changing its shape (Truesdell, 1991). In Figure 14, a Schoeller diagram for water from ten thermal wells and one cold well (no. 72) clearly shows bicarbonate waters. As seen, there is no clear movement in the connected line for some analyses to suggest mixing thermal waters with cold groundwater.

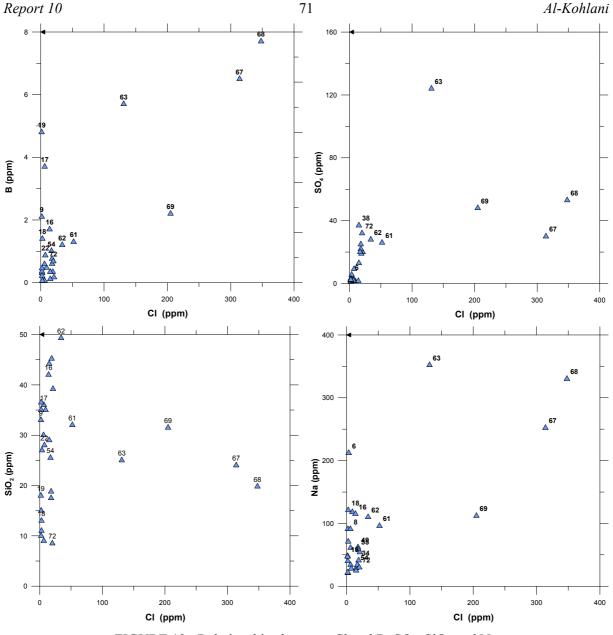


FIGURE 13: Relationships between Cl and B, SO<sub>4</sub>, SiO<sub>2</sub> and Na for the Al-Lisi – Isbil wells

# 4.5 Mixing models

Normally the solution reactions and mineral exchange tend to re-equilibrate with cooling, but much slower at lower temperature, so when applying mixing models to estimate subsurface temperatures, several simplifying assumptions are made. Conservation of mass and heat is always assumed, both during and after mixing. Therefore, it is assumed that chemical reactions occurring after mixing are insignificant and do not modify the water composition. Mixing models have been developed to allow for the estimation of a hot water component in mixed waters in springs or discharge from shallow drillholes. In other words, the combined heat contents of two waters at different temperatures are conserved when waters are mixed, but the combined temperatures are not; the enthalpy is used as a coordinate rather than the temperature. Under this principle, dissolved silica concentration versus enthalpy can be applied to determine the temperature of the hot water component.

Silica-enthalpy mixing model: Truesdell and Fournier (1977) proposed a simple model that is a plot of dissolved silica versus the enthalpy of water to estimate the temperature of the deep hot water

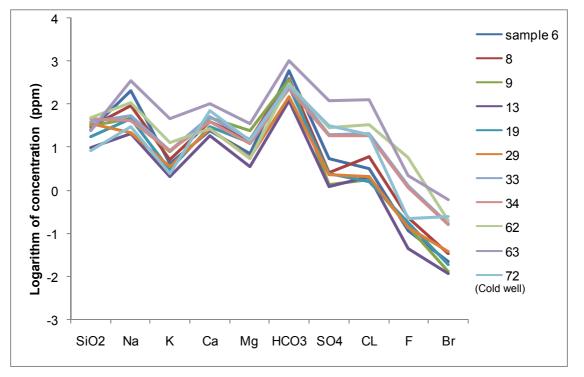


FIGURE 14: Schoeller diagram for the Al-Lisi – Isbil well samples

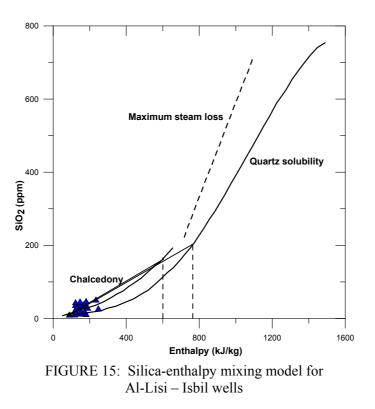
component. This model is based on the assumption that no conductive cooling occurred after mixing. If the mixed water cooled conductively after mixing, the calculated temperature of the hot water component would be too high. It is also assumed that no further silica solution and deposition occurred before or after mixing. There are some criteria for hot spring waters which may be appropriate for the application of this model:

- A measured water temperature which is at least 50°C less than calculated silica and Na-K-Ca geothermometer temperatures;
- A silica geothermometer temperature which is lower than the Na-K-Ca temperature; and
- A mass flow rate which is high enough to allow for only a minor conductive cooling.

This model cannot be used for boiling springs because heat is carried away in the steam after mixing.

The silica-enthalpy mixing model was applied to the data from the Al-Lisi – Isbil geothermal field (Figure 15). Almost all plotted samples tend to cluster at one point, very close to and above the quartz solubility line. It means these samples may not be appropriate for the estimation of the reservoir temperature. However, two lines of mixing were drawn, according to the distribution of the other data points. The upper line between the cold water and the mixed thermal water intersects the chalcedony solubility curve where enthalpy is equal to 600 kJ/kg, and corresponds to the estimated reservoir temperature, 143°C. This is higher than the calculated temperature estimated using the chalcedony geothermometer. The lower (black) line intersects the quartz solubility curve where enthalpy is approximately 785 kJ/kg, giving an estimated temperature from 120°C to 185°C. This estimated temperature of 185°C is similar to the results from the Na/K geothermometer, indicating that most of the hot waters have mixed with cooler water in the reservoir or conductive cooling probably occurs during the upflow of the hot waters.

72



# 5. CONCLUSIONS

Exploration of geothermal sources in Yemen has been conducted since 1982 and scientific studies have been carried out since 2001 to assess the energy potential and possible use of geothermal energy for direct and indirect utilization in Yemen; until recently, these sources were only used in tourism, bathing and for irrigation purposes.

Water samples from 29 wells in the Al-Lisi – Isbil geothermal field were analysed and studied using geochemical methods. The chemical composition of the geothermal water in the study area is rich in Na and HCO<sub>3</sub> and classified as peripheral water that may have mixed with cold groundwater or  $CO_2$  from a magmatic source.

The computer program WATCH 2.3 was applied for the interpretation of the chemical composition of the geothermal fluids. The program was used for the calculation of aqueous speciation, the evaluation of mineral equilibrium in the fluid and the estimation of reservoir temperature. Reservoir temperature was estimated using several geothermometers and the results were then compared. The maximum reservoir temperature was predicted to be between 100 and 150°C in the study area.

The possibility of mixing samples with cool groundwater was evaluated by different geochemical methods such as the Schoeller diagram and the investigation of a linear relationship of chloride anions with other constituents. These methods indicated that there is evidence of mixing with cold water.

Evaluation of mineral saturation indices of different minerals indicates that none of the minerals are in equilibrium. Thus, no definite mineral equilibrium temperature can be observed. It also indicates that most minerals are undersaturated and the risk of precipitation is low. However, it must be noted that the calculation of equilibrium conditions was restricted due to the lack of aluminium measurements.

Exploration drilling is recommended for more detailed studies in this area to identify temperature at depth, as well as modelling, deep water sampling and the measurement of more components in water samples.

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