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Geothermal Geochemistry Based on Alteration Mineralogy and Fluid Inclusion Microthermometry of Hes-Daba Area in Gagade, Republic of Djibouti

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ABSTRACT

Fluid inclusions from the Hes-Daba area were studied. Microthermometric measurements were made on quartz collected from the surface veins, which hosted two phases (liquid+ vapor) inclusions. Mean homogenization temperature ranges from 150 °C to 367 °C and ice-melting temperature ranges from −0.05 °C to − 1.14 °C indicating that inclusion solutions consist of 0.1 to 1.9 eq. wt% NaCl. For estimating formation temperature, evaluating thermal history and thermal structure. Selected samples have been analyzed with XRD to provide direct information on geothermal reservoirs, because geothermal fluids, through their interaction, can alter the composition and properties of rocks. The main alteration minerals are quartz, calcite, alunite, epidote, hematite and clay minerals (illite, smectite and chlorite). Therefore, the clay constitutes a transition to a high-temperature environment which is evidenced by high-temperature hydrothermal alteration minerals such as quartz (>180°C), and epidote (~250°C).

1. INTRODUCTION

Republic of Djibouti is situated in the Afar depression which occurs at the junction of three rifts (Red sea rift ,Gulf Aden rift and East African rift).Italian National Research Council(CNR) and French National Center for Scientific Research(CNRS) conducted studies in the Afar area in detail in the 1970s and concluded the existence of spreading axes similar to oceanic rifts in the Afar. In the context of volcanism and extensive tectonism since 25 Ma, volcanic rocks mainly cover the Republic of Djibouti. These volcanic series have erupted during different phases of expansion and are: Adolei basalt (25Ma), Mabla rhyolite(15Ma), Dalha basalt 9(Ma), Ribta rhyolite(4.25Ma), Stratoid basalt (3.3 Ma), Gulf of Tadjoura basalt (3.1 Ma), Recent rifts basalt (Holocene to present). Extensional tectonic phases and related volcanism have created numerous geothermal systems in the republic of Djibouti. The most tectonically active structure in Djibouti is the Assal rift. The first geothermal exploration in Djibouti was then conducted by the French Geological Survey(BRGM) in the 1970s. The studied area of Hes-Daba is located in the Gaggade region of the currently active Great East African Rift, which is opening up at the rate of 10-15 mm/year. In order to reveal and clarify the geothermal structure of Hes-Daba, 18 surface samples were collected for a fluid inclusion study and hydrothermal alteration mineralogy. The main aim of these studies is estimating formation temperature, evaluating history of thermal activity and thermal structure. Finally, evaluate geothermal systems and understand geothermal reservoir zones.

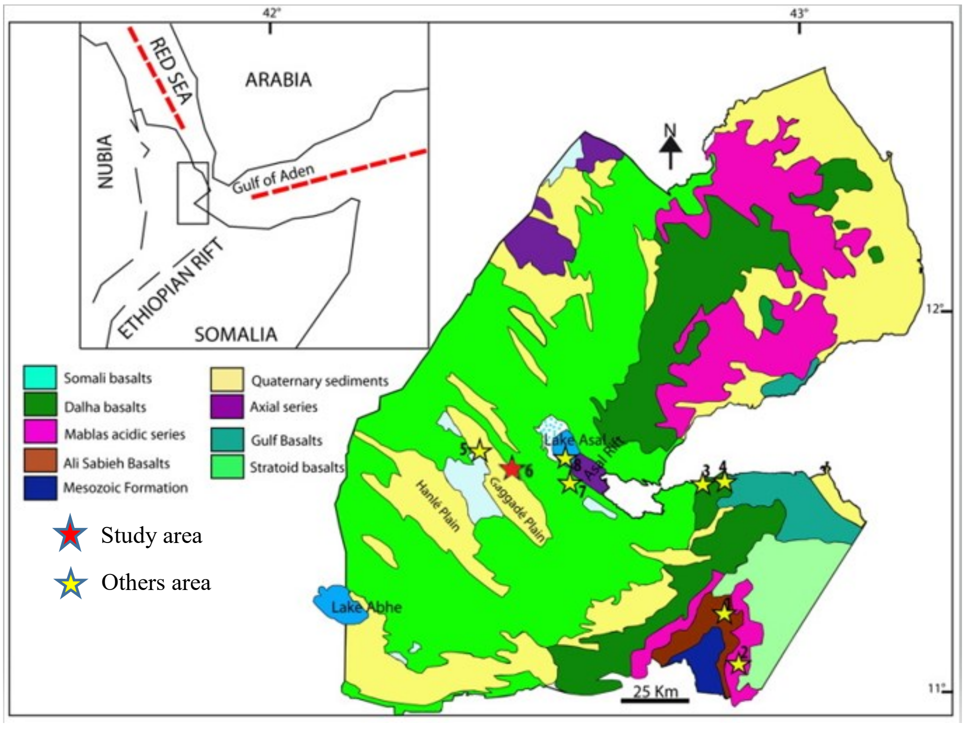


Figure 1: Geological map of republic of Djibouti (Moussa et al., 2012)

2. GEOLOGICAL SETTING

Most of the country is composed of Cenozoic sedimentary and volcanic rocks as shows in Figure1. It is located at the junction of three major rifts: the continental Great East African rift, the Gulf of Aden Rift and the Red Sea Rift. The triple junction is in the Afar region of Djibouti and Ethiopia. This area represents a region of stretching, exposing oceanic crust and extrusive flood basalts that proceeded rifting. The Hes-Daba area is located between the Gaggade and Asal faulted depressions, in one of the felsic extrusions interstratified in the intermediate member of the 3.3–1 Ma Stratoid series basalts. There are several parallel NW-SE trending, steep northeasterly dipping normal faults, transecting the sub horizontal SW dipping basaltic rocks. Most of mineralization are observed in a network of two km long rift-parallel veins cutting through dominantly trachytic lavas (Moussa et al., 2012).

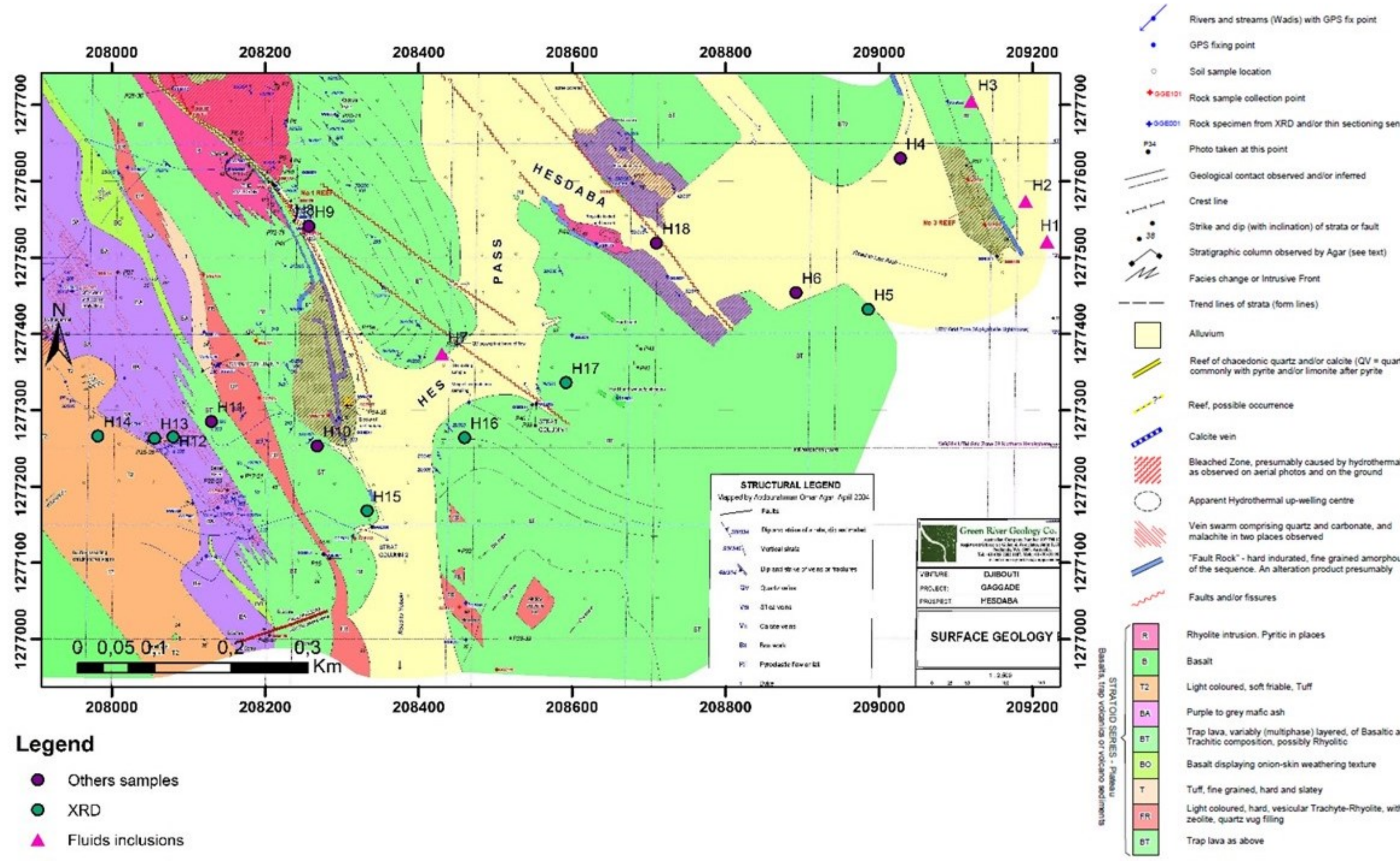


Figure 2: Location map of the samples

Figure 2 shows the location of sampling point (H1 to H18) in the study area. Most of the samples were collected from quartz veins. Orientation and physical property of the outcrop were measured in the field.

3. METHODOLOGY

3.1 Fluid Inclusions

Fluid inclusions are small volumes of paleo-fluids (liquid, gas or solid) trapped in minerals. There are two types of fluids inclusion, primary and secondary fluids inclusions when the fluids are trapped along the growth zones and crystal faces, or tends to occur solitary or isolated. These are good indicators of the condition of crystallization of host minerals. On the other hand, secondary fluid inclusions indicate the fluids trapped in the fractures, which are developed after the formation of host mineral and caught due of healing of fractures. The study of fluid inclusions provide main information such as temperature, pressure, salinity, density and chemical composition of the fluids.

3.1.1 Sample Preparation

Sample preparations for fluids inclusion analysis need a lot of caution and time. Rock samples are polished several times with different materials of different sizes (powders, discs). The step is first to cut the samples with the isometric cutter, then, the sample is polished until having flat surface. Then stick the samples on the glass plate with glue and leave for 7hr to attach. Subsequently cut the other side of the samples and remake the polishing with discs and powders up to the size of the normal thin section, which is about 3 x 5 cm and the ideal thickness, should typically be between 90 and 120 µm, depending on transparency of the host crystal and the inclusion size and abundance, are very important factors. Figure 3 presents picture of preparation steps.

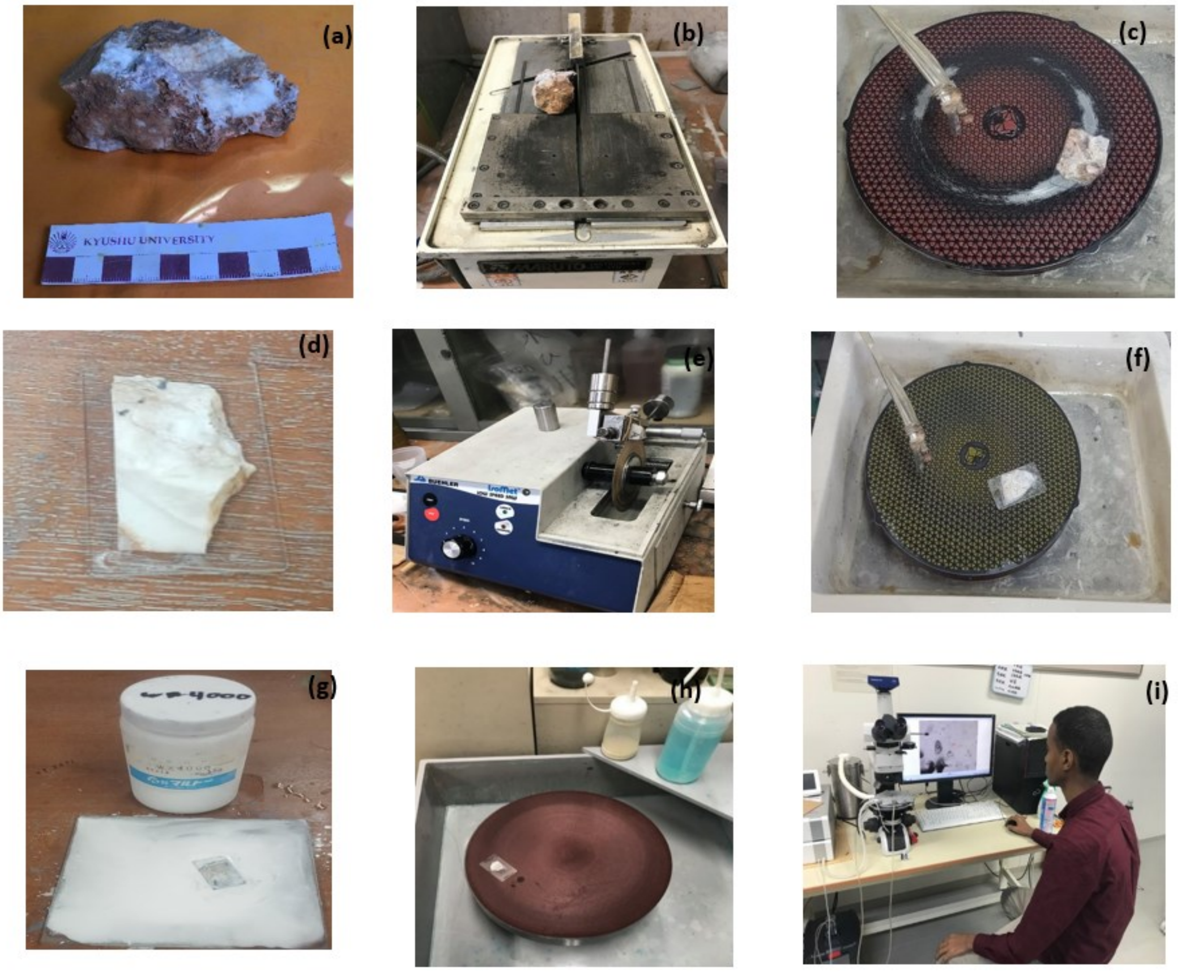


Figure 3: Fluids inclusions and instrumentation (a) rock sample, (b) cut the sample with the cutter, (c) polish the sample, (d) stick the sample on the glass plate, (e) cut the sample with the isometric cutter, (f) polish the other side of the sample, (g) polish with the powder 4000, (h) diamond polish, (i) measurement of fluid inclusions microthermometry

3.2 XRD Analysis

X-ray diffraction (XRD) analysis can identify secondary minerals formed by geothermal activity. Creation of secondary minerals depends on fluid temperature, water chemistry, type of host rocks.

3.2.1 Sample preparation

In the laboratory two type of powdered sample, namely bulk sample and oriented sample were prepared for the XRD analysis. The objective of the bulk sample analysis is to identify quickly the constituent of the sample. To perform the XRD analysis, ground powder sample must be prepared and with great care to avoid contamination. For the bulk sample preparation the sample are crumpled into smaller pieces and dried in an oven at 45 ^{o}C for one day to remove the moistures from the sample and then the sample are crushed into the powder size. Finally powdered sample are compressed on a metal plate as thin film so that XRD can analyze properly to determine altered minerals.

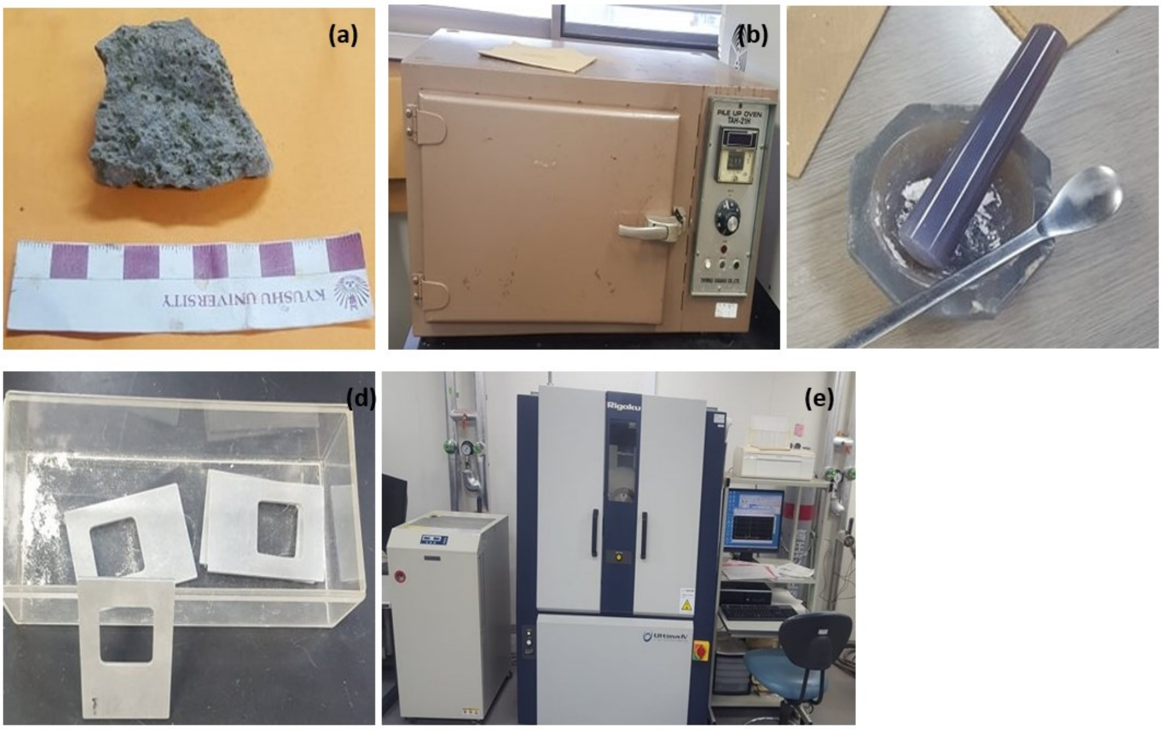


Figure 4: Bulk sample preparation and instrumentation (a) rock sample, (b) oven, (c) mortar and pestle, (d) compressed powder specimen on metal plat, (e) Rigaku XRD machine.

The oriented sample was prepared for collecting and identify clay mineral from the rock sample. Due to fragile nature of clay mineral at high temperature, drying in an oven was avoided. Then crushed sample is immersed into de-ionized water in beaker, let it stay in ultrasonic shaker for 30 min to dispense, and suspends clay mineral in the solution. Then solute began to precipitate according to the specific density. After around 3hr the clay mineral appeared in the upper part of the solution was collected and centrifuged to collect concentrated clay mineral at the bottom of tube. Clay minerals were dropped on a glass blade and then air dry for 24hr before the analyses with XRD.

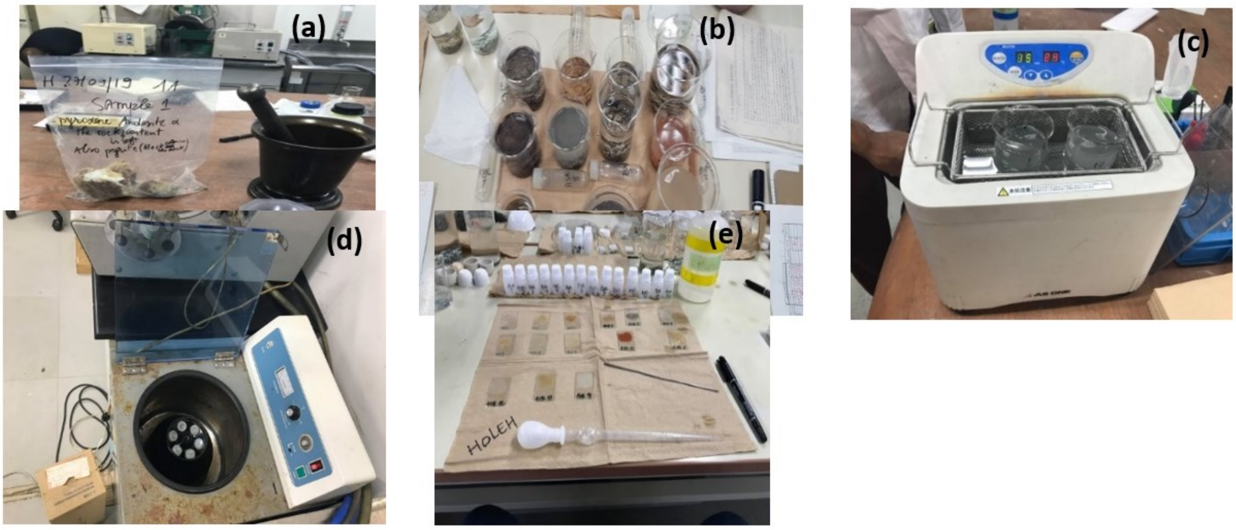
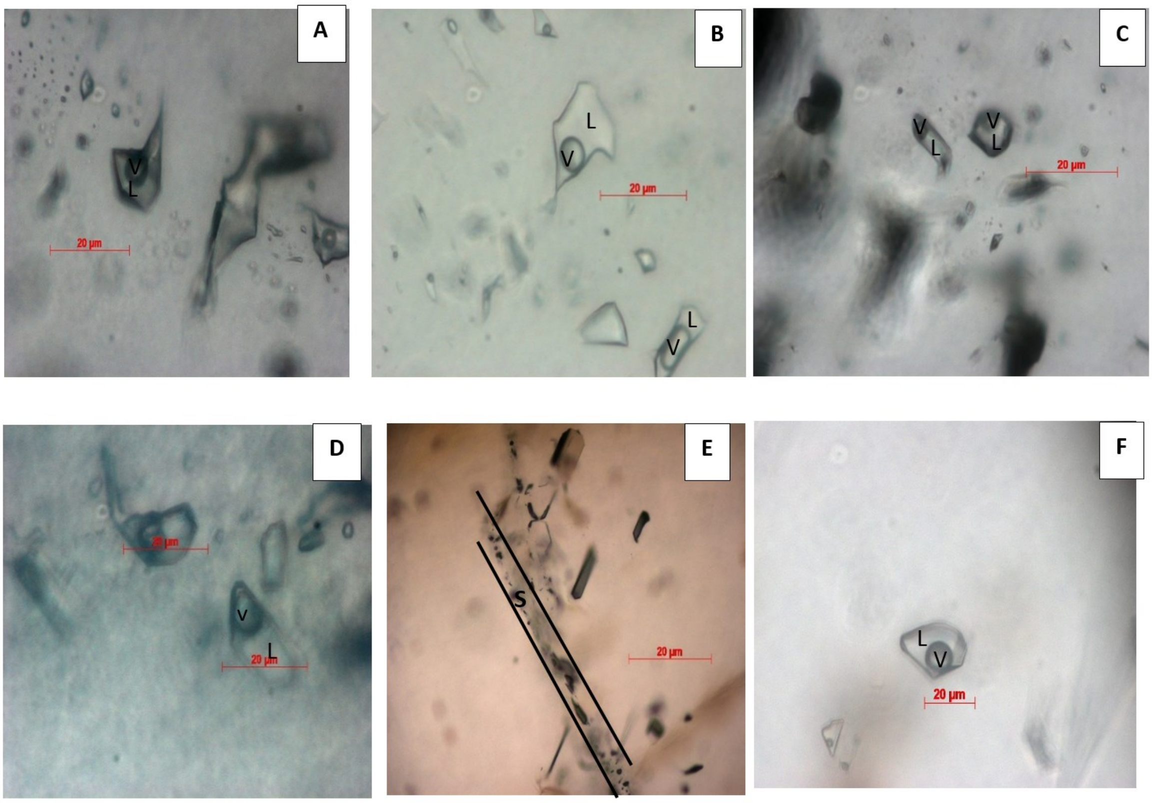


Figure 5: Oriented sample preparation and instrumentation, (a) Crash the sample to powder size, (b) Samples in the beaker to suspend clays on the top, (c) Samples set in ultrasonic shaker, (d) Centrifugal to precipitate clay, (e) orientation sample

4. RESULTS AND DISCUTION

4.1 Fluids Inclusion Petrography

Figure 6 shows photos of the inclusion of fluids found in samples H7 and H9. Photos A, B, C, D, and E present the fluids inclusion that were found in the sample H7 and the photo F in sample H9.



Figures 6.Photomicrographs of fluids inclusions types quartz veins from the Hes-Daba prospect, L=Liquid and V=Vapor, primary fluid inclusion (A, B, C, D, F) and secondary fluid inclusion (E)

Inclusion size varies from 10 to 20 µm, and most inclusions are rectangular or rectilinear; a small subset are round, appearing circular in cross section and two types of fluid inclusions were identified in quartz: liquid-vapor with liquid rich, variable degree of filling and another type vapor-liquid with vapor rich. The most common are L-V, liquid-rich, with homogenization temperatures ranging from 150°C to 367° C.

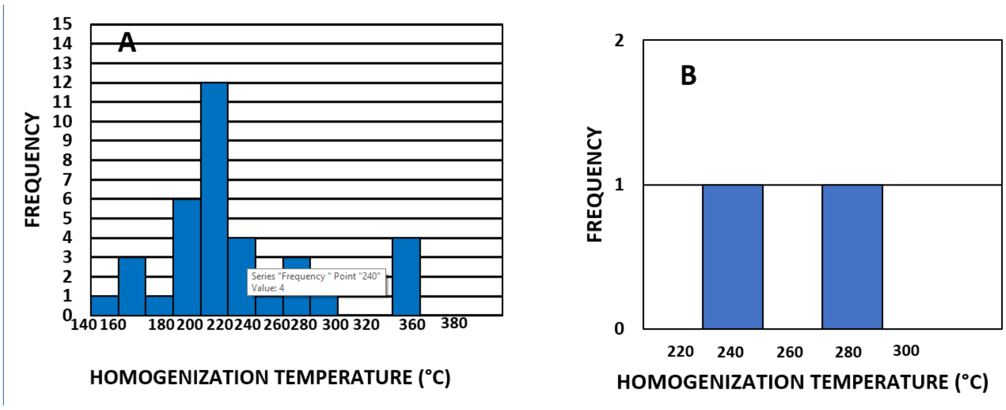


Figure 7. Frequency histograms of homogenization temperatures for fluid inclusions in quartz veins of samples, A for H7, B for H9

Figure 7 represents the frequency histograms as a function of homogenization temperature of samples H7 and H9. Thirty seven(37) fluids inclusions were found in the sample H7 and two(2) in the samples H9. During heating of a liquid-rich inclusions , the vapor bubble volume decreases continuously and smoothly with increasing temperature until homogenization occurs. Homogenization temperature with highest frequency is 225° C for H7.

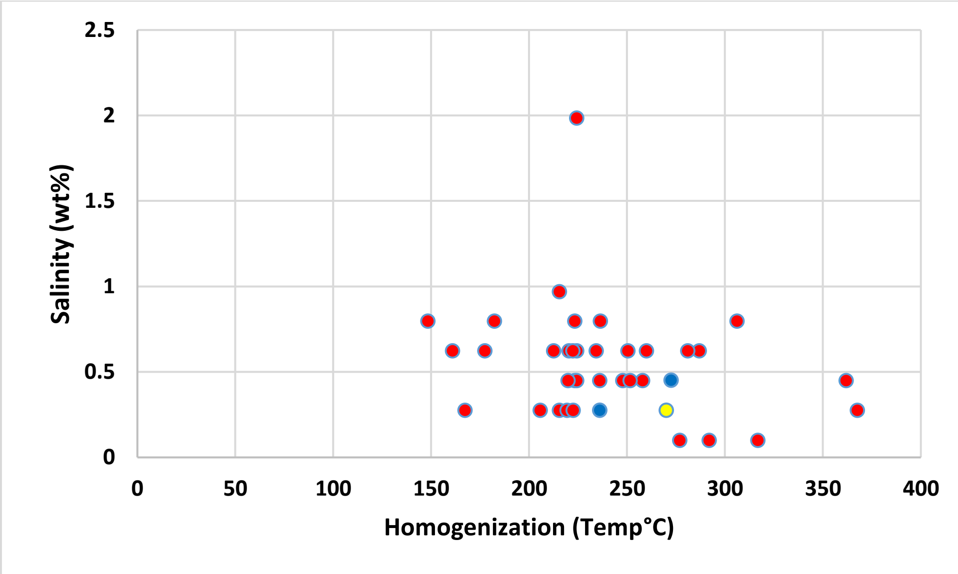


Figure 8. Salinities for fluid inclusions in quartz veins from Hes-Daba (H) and homogenization temperature for Sample H2(yellow), H7(red), and H9(blue).

Salinity of the inclusion was calculated using freezing-point depression temperatures with the equation proposed by Bodnar(1994) :

$$\text{Salinity} = 0.00 + 1.78Ø - 0.0442Ø^2 + 0.000557Ø^3$$

where Ø is the depression of the freezing point in degrees Celsius.

Figure 8 shows relations between the salinity and homogenization temperature for the samples of H2, H7 and H9. The salinities are relatively uniform ranging from 0.1 weight % to 1.9 wt. % NaCl equivalent.

Primary fluid inclusions in the crystal of quartz veins from Hes-Daba have a little low melting temperature corresponding to low saline brine at the temperature in the range of 150 ° to 367°C. The homogenization temperature of inclusions ranges from 150°C to 367°C require either deep circulation of originally hot surface water, as might be expected if circulation involved major fault in the underling crystalline basement. In general, surface quartz vein is considered to be created at subsurface in the past. Due to surface erosion probably with uplift, the formation at subsurface have been exposed to the surface. Therefore, homogenization temperature of fluid inclusion of quartz vein obtained at the surface shows fluid temperature trapped in the quartz at subsurface. When spatial distribution of homogenization temperature of fluid inclusion at surface is obtained, past temperature distribution and center of geothermal activity can be estimated. The low salinity of the solutions and the absence of CO_2 and minerals (e.g. halite) suggest that the main component is meteoric water. Based on these results and the previous study (Moussa et al., 2012), we can suggest that two types of hydrothermal fluids have contributed in this area: the meteoric water or magmatic water diluted by meteoric water.

4.2 XRD Results

Figure 9 shows the results of XRD analysis for the sample (a) H5 and (b) H12. Results are summarized in Table 1. Based on the results of XRD analysis, the alteration minerals found in this area are mainly quartz, calcite, alunite, epidote, and clay minerals (chlorite, smectite, illite). Quartz occurs either as an alteration product of opal or chalcedony or as a vesicle or vein filling mineral (Moussa and al., 2012). It is generally associated with epidote, prehnite, pyrite and calcite (Gebrehiwot, 2010). Epidote is an abundant and common mineral formed in geothermal systems. The occurrence of epidote in significant quantities indicates temperatures above 240-250ºC (Kristmannsdóttir, 1979) and it has a distinctive yellowish to greenish colour.

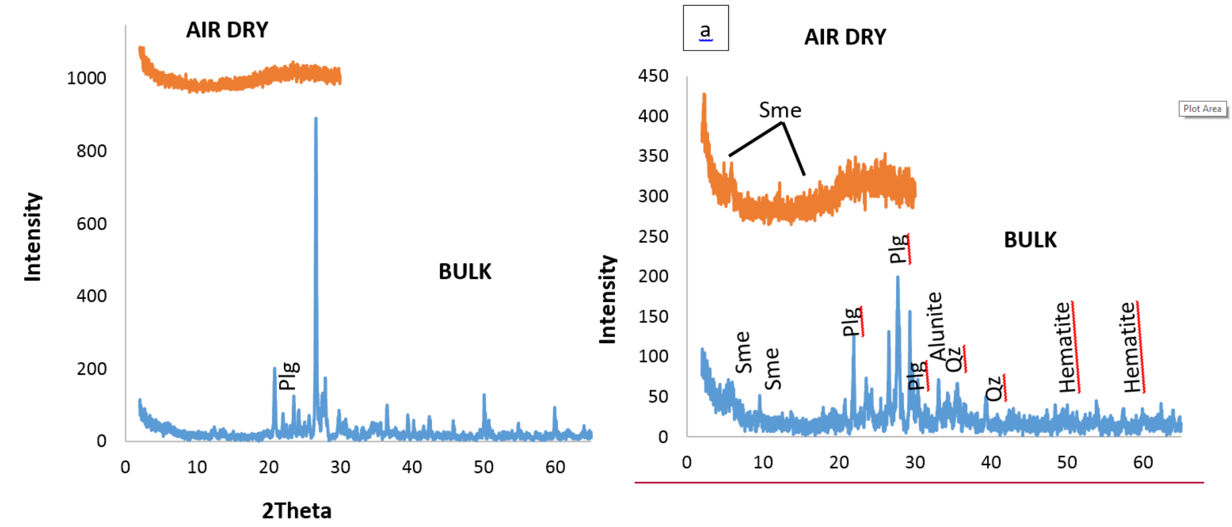


Figure 9: XRD pattern of bulk sample and oriented sample (Air-dry) a) H5 and b) H12.

Table 1: Minerals identified in samples from Hes Daba.

Mineral / Sample	Plg	Calcite	Quartz	Alunite	Chlorite	Vermiculite	Illite	Smectite	Serpent	Hematite	Wollastonite	Epidote
H5	xx		xx		x		x					
H12	xx	x	xx	x			x			x		
H13	xx			x				x	x	x		x
H14	xx		xx			x		x				
H16	xx	x	xx				x			x	x	
H17	xx	x			x			x		x		x

Calcite is a common and widespread mineral filling veins and vesicles. It is white to colorless under binocular microscope, but transparent to translucent with perfect cleavage in the petrographic microscope. It is a colorless to white or cloudy (milky) and transparent to translucent mineral. Plagioclase(Plg) is the most abundant mineral occurring in most igneous rocks and a major mineral in basalt. Clay minerals are widely used as the best tool in geothermal exploration as temperature indicators (Kristmannsdóttir, 1979). Smectite is the clay mineral with the lowest formation temperature. It is formed from the alteration of glass or primary minerals like olivine and forms directly from water rock interaction, precipitating into voids and veins. Smectite is an indicator of temperatures lower than 200ºC. Chlorite occurs both as a replacement of primary minerals in the rock and as void fillings. Chlorite is an indicator of temperatures exceeding 230°C (Kristmannsdóttir, 1979).

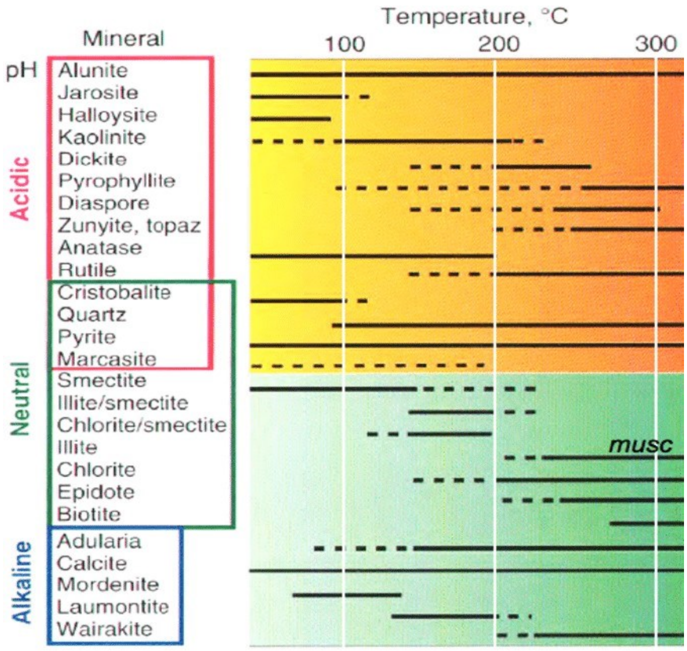


Figure 10: Variation in mineral stability with temperature at quartz solubility (dashed line for stability at amorphous silica solubility). Modified from Hedenquist et al. (2000).

According to these results, the presence of clay minerals such as smectite and illite indicate that hydrothermal alteration in this region is acidic to neutral. While those samples with clay mineral of chlorite calcite and illite indicate that, it is neutral to alkaline type. The presence of chlorite, alunite and epidote show formation temperatures is higher than 230°C.

5. CONCLUSION

The primary fluid inclusions in the crystal of quartz veins from Hes-Daba have a little low melting temperature corresponding to low saline brine (0.1 and 1.9 wt %) in the temperature range of 150 ° to 367°C. The high salinity cause deposition of minerals in surface facilities but in the case of Hes-Daba with 0.1 and 1.9 wt % of salinity is not so high and has no negative effects for geothermal exploration. Based on the XRD analysis, the alteration minerals in this area are mainly quartz, calcite, clay minerals (smectite, chlorite, illite), alunite, epidote, hematite, wollastonite and serpentine. This results in the formation of hydrothermally altered minerals, some of which are known to form at specific and stable temperature regimes. The clay constitutes a transition to a high-temperature environment which is evidenced by high-temperature hydrothermal alteration minerals such as quartz (>180°C), and epidote (~250°C). Therefore, the results of fluid inclusions and XRD give a good indication of the evolution of the geothermal system in the Hes-Daba area.

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