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Mineralogy, Geochemistry and Volcanology of Volcanic Tuff Rocks from Jabal Huliati Al-Gran, South of Jordan (New Occurrence)

Reyad A. Al Dwairi^{1)} and Suhail I. Sharadqah¹⁾*

¹⁾ Tafila Technical University, Engineering Faculty, Natural Resources and Chemical Engineering Department,
P.O. Box (179), Code (6611), Tafila, Jordan.

* Corresponding Author. E-Mail: reyadn@hotmail.com

ABSTRACT

Jabal Huliati Al-Gran (HG) volcano is one of several volcanic eruptions belonging to south Jordanian basaltic eruptions. Thick pyroclastic deposits of volcanic tuff layers alter slowly to complex mineralogical zonations in closed hydrological alkaline environments, and relatively pure deposits can be formed. Hydrological system and temperature are the principal controls over the zeolitization process. This process involves reactions between the vitric silicic volcanic glass and the percolating water in a closed hydrological system to form distinctive zeolite assemblages. Judging from field and experimental data, formation of phillipsite, chabazite and other secondary rock forming minerals probably took place by reaction of percolating water with vitric tuff units.

The petrographical, mineralogical and geochemical investigations include thin section, XRD and SEM-EDX to determine the nature, geneses, along with mineralogical and geochemical properties of this new zeolitic occurrence.

This work reveals the presence of zeolites in Huliati Al-Gran tuffaceous materials. Also, the results indicated that the volcanic tuff is highly altered to zeolites and other minerals. The main zeolites are phillipsite Ca-heulandite (mean Si/Al: 3.30) and chabazite Ca-clinoptilolite (mean Si/Al: 4.35). Zeolite minerals compose 10–60% of the whole volcanic tuff rocks.

Thermal analysis indicates high stability for temperature difference. The deposit might be of great importance for Jordan, considering its enormous zeolitized outcrop area. However, the quantitative estimation still needs further investigation.

KEYWORDS: Natural zeolite, Mineralogy, Volcanic tuff, Phillipsite, Jabal Huliati Al-Gran.

INTRODUCTION

Zeolites are crystalline, hydrated aluminosilicates of alkali and alkaline earth cations that possess infinite three-dimensional crystal structures. They are further characterized by an ability to lose and gain water reversibly and to exchange some of their constituent

cations without major change of structure, enclosing pores occupied by cations and water molecules, permitting reversible ion exchange and reversible dehydration. Zeolites are mostly found as a weathered white material filling the pyroclastic vesicles of volcanic rocks (Cooney et al., 1999).

Volcanic tuff is an igneous rock composed of volcanic glass fragments, and is the most suitable host

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material for natural zeolites because of its ease of chemical reactivity. On the national scale, zeolitic tuff occurrence, geneses, geochemistry and uses have been subjects for numerous studies. The first study in Jordan which reported the presence of natural zeolites was carried out in the mid eighties of the past century (Dwairi, 1987). That study indicated that the most common zeolite mineral in Jabal Aritayn area is phillipsite. The mineral is an alteration product of volcanic glass.

Later on, a lot of mineralogical and geochemical studies have been carried out on Jordanian volcanic tuffs and natural zeolites such as: Dwairi (1993 and 1996), Ibrahim (1996), Khoury et al. (2003), Al-Malabeh (1994), Al-Malabeh (2003), Al-Malabeh et al. (2003), Ibrahim and Al-Malabeh (2006) and El-Hasan and Al-Malabeh (2008). Most of the above previous studies focus on northeast basaltic Plateau (Harrat Ash-Sham Basaltic Super Group), especially Jabal Aritayn. These studies led to discover several new zeolite locations in northeast Jordan and helped to describe new paragenetic sequences for the authigenic zeolites of Jabal Aritayn formation as follows: [fresh sideromelane → palagonite → smectite → faujasite → phillipsite → chabazite → natrolite → calcite] (Ibrahim, 1996).

Al-Dwairi (2007) explored and studied the characterization of all possible locations of volcanic tuff in Jordan. He studied mineralogy, petrology and geochemistry of all volcanic tuff localities (north east, central and south Jordan). Also, he studied (2009) the mineralogy and authigenesis of zeolitic tuff from Tall-Juhira and Tall Amir, south Jordan.

Al-Dwairi et al. (2010) studied the occurrences and properties of Jordanian zeolites and zeolitic tuff, establishing a database for Jordanian zeolites to be used by researchers.

Most volcanic eruptions in south Jordan have never been studied or evaluated for their mineralogical or chemical composition. Jabal Huliati Al-Gran volcano is one of the most important localities that haven't been studied. The main objective of this research paper is to

investigate the presence of zeolitic minerals in the tuff materials of Jabal Huliati Al-Gran, south Jordan.

GEOLOGICAL SETTING

Jabal Huliati Al-Gran is located within the basaltic eruptions along the arched eastern rim of Jordan graben, south of Jordan (Bender, 1974). The south Jordan volcanic eruptions belong to volcanic eruptions in north east Jordan (Harrat Ash Shaam) (Ibrahim et al., 2003). Jabal Huliati Al-Gran volcano is situated about 30 km east of Al-Tafila city (Fig. 1). Huliati Al-Gran has two peaks, so it might be referred to each one as a separate mountain. The height of the northern peak is 1331m and the height of the southern one is 1341m above sea level.

To address the regional tectonic framework, and based on previous models of Gregoy et al. (1982), Ibrahim (1993) proposed that the history of Cenozoic basaltic volcanism in Jordan can be explained by considering the relative plate movement of Africa and Arabia and the close association of the eruptive centers with regional faults. This close association is still valid on the local scale.

The Arabic name of Huliati Al-Gran means that the two Huliati mountains are conjugate. The geological field study shows that what is suggested in the Arabic name for Huliati Al-Gran is almost correct. Both mountains have been a source for basaltic materials (Fig.2).

Both mountains have a crater close to the top of the old mountain, and in both cases the basaltic materials partially cover the mountain, but almost conserve its original shape.

For the southern mountain, at least one explosive eruption stage has been distinguished, while for the northern one two stages were clearly observed. The first stage which is rich in pyroclastic almost covered the mountains themselves. In the second stage, the basalt flowed from the north Huliati for eleven kilometers following the existing hydrological pattern. The basalt of the second stage covers about 10 km².The

geological map (Fig. 3) and the two cross-sections (Fig. 4) show the extensions and the geological

positions of the basaltic flows of Huliati Al-Gran.

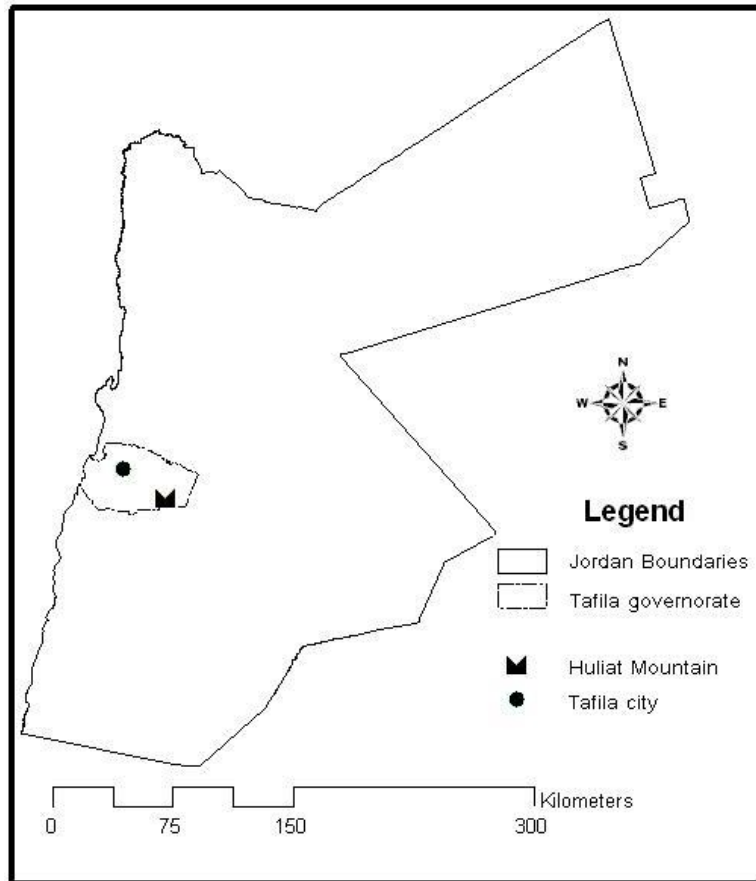


Figure (1): Location of Jabal Huliati Al-Gran volcano, south Jordan



Figure (2): A photo showing two separate mountains belonging to Huliati Al-Gran volcano

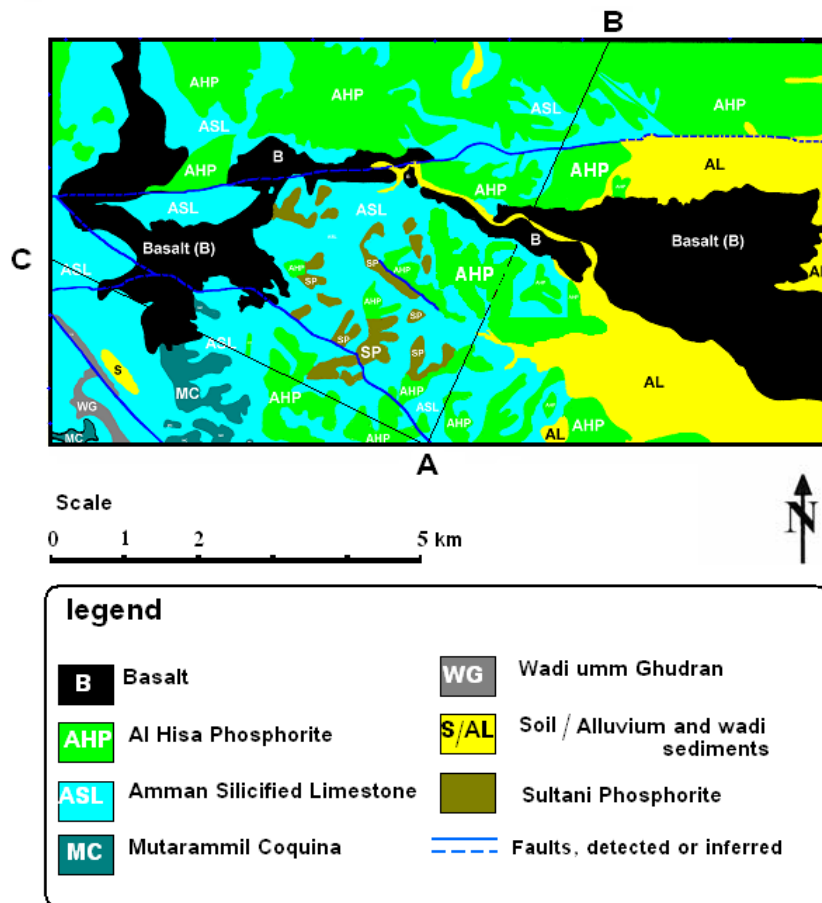


Figure (3): Geological map of the study area

Age of Jabal Huliati Al-Gran

The basaltic eruptions along the arched eastern rim of Jordan belong to Cenozoic volcanism (Bender, 1974). The flows located west of Jurf Ed Darawish railway station overlay a conglomerate unit to which is assigned an age of middle pleistocene (Bender, 1974). 20 km south-west of the study area, two basaltic flows are separated by about 20 m of gravel and conglomerate which have a similar middle pleistocene age. These flows are found overlying the Dhira Ebn Saleh Conglomerate which is of Miocene to Pliocene age. Assuming the same age for close eruptions, it becomes acceptable that the basaltic volcanism of Jabal Huliati Al-Gran is of Pliocene-Pleistocene age.

METHODS OF STUDY

The volcanic tuff samples were collected along measured stratigraphic sections from various locations from Jabal Huliati Al-Gran. Mineralogical and geochemical studies were conducted on 32 samples. The mineral content of the whole rock samples and their sizes were determined by optical microscopy and X-ray diffraction (XRD) analysis. X-ray diffraction was performed on a Phillips PW 340 Diffractometer operating at 40 kV and 30 mA using Cu-K α radiation.

Micromorphologic properties of zeolitic tuff samples were observed on Scanning Electronic Microscopic (SEM) Quanta 600 F, FEI combined with Energy-Dispersive X-ray analysis (EDX) mapping

(Genesis 4000, EDAX) available in the Federal Germany.
 German Geological survey (BGR), Hannover,

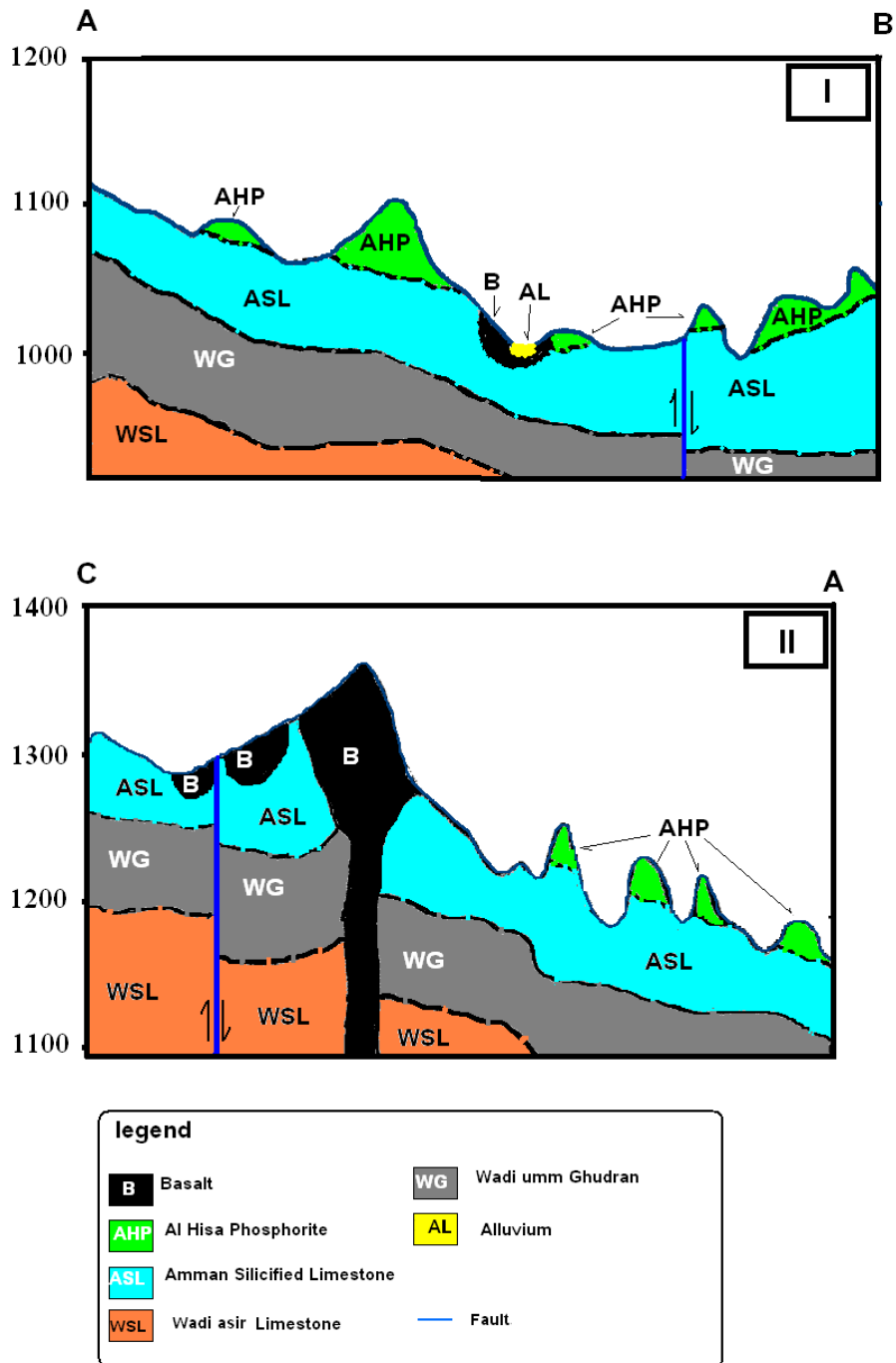


Figure (4): Two cross-sections showing the geological positions of basaltic flows from Huliati Al-Gran Mountains (The direction of the 2 cross-sections is shown in Figure 3)

Major elemental analyses of the samples comprising SiO_2 , TiO_2 , Al_2O_3 , total Fe_2O_3 , CaO , MgO , Na_2O , K_2O were carried out using X-ray fluorescence (XRF) techniques. The used apparatus is (Axios-PAN Analytical) available in the Federal German Geological Survey (BGR), Hannover, Germany. Fusion tablets were prepared for XRF analysis.

The dehydration of zeolite processes is important in a variety of applications including pollution abatement, catalysis and gas separation. Thermal analysis comprises a group of techniques in which a physical property of a substance is measured as a function of temperature. Thermal analysis involves heating or cooling a test sample. Differential thermal and thermogravimetric (DTA-TGA) analysis were carried out using simultaneous thermal analyzer (STA 409 PC) Luxx apparatus. Differential scanning calorimeter (DSC) apparatus either was used to study the thermal behavior of Jordanian zeolitic tuff. Thermal analysis was carried out at the laboratories of the Chemistry Department at the University of Jordan.

RESULTS AND DISCUSSION

Thin Section Petrology

Three thin sections for each sample were prepared in this study. The results show that the palagonite glass material is a major component with some secondary filling material in the vesicles (Fig. 5). Olivine and pyroxene are the most important rock forming minerals within the palagonite glass in the samples. The altered filling materials are composed of zeolites, calcite and smectite. Calcite occurs in the form of coarse-grained cement-filling central parts of vesicles and the intergranular spaces in the majority of the studied thin sections. Zeolites formed rims of radial growth phillipsite crystals. The presence of secondary rock forming minerals indicates the breakdown of rock-forming primary minerals during weathering as alteration products. Willson (2004) described the weathering of pyrogenic minerals and their alteration products. He found that olivine, plagioclase and pyroxene break down during weathering to clay minerals, Fe oxides, as well as Ca, Na and K aluminosilicate rich minerals.

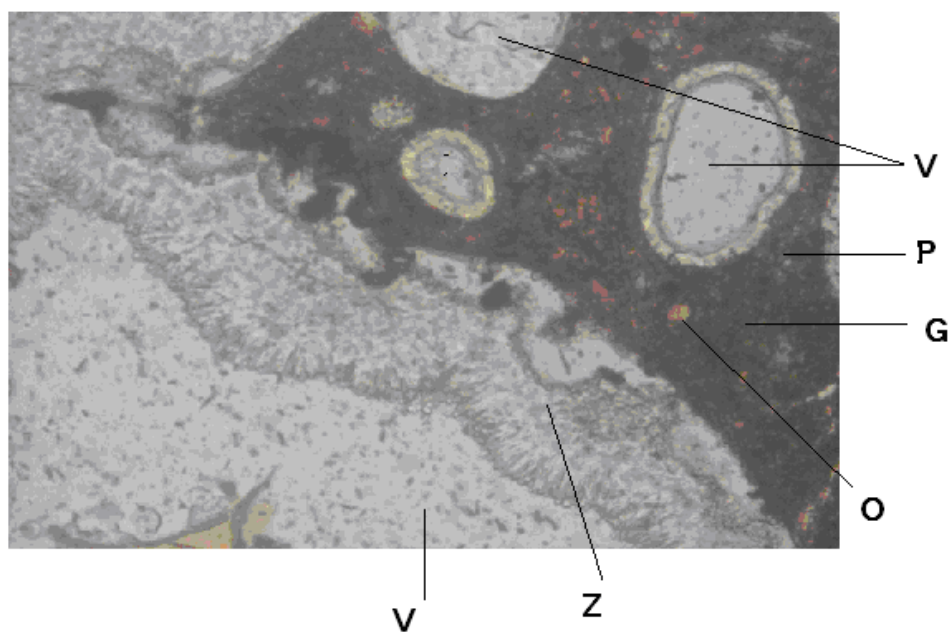


Figure (5): Photomicrograph of palagonized tuff showing: V- Vesicles, P- Pyroxene, G- Glass, O- Olivine, and Z- Zeolites

Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray (EDX)

The SEM micrographs of Jabal Huliati Al-Gran zeolitic tuff for polished samples are shown in Figures 6 and 7. SEM micrographs for zeolitic tuffs show that they grew directly on the wall of the palagonite (Fig. 6). Phillipsite is the major zeolite mineral appearing in the photomicrographs, phillipsite crystals grow in groups as spherulitic radiating prismatic crystals. The individual phillipsite group consists of rosiest crystal

shape (radial crystal form) (Fig. 7). EDX analysis for phillipsite crystal from Jabal Huliati Al-Gran, south Jordan is illustrated in Figure 8. The results show that the phillipsite crystal has variable amounts of O, Si, Al, Na, K, and Ca with a high content of Na, K and Ca. The presence of the elements above indicates that the chemical composition of phillipsitic crystals is (K, Na, Ca) (Si, Al) 8 O16. The results agree with the EDX results for Phillipsite from south Jordan obtained by Al-Dwairi (2007).

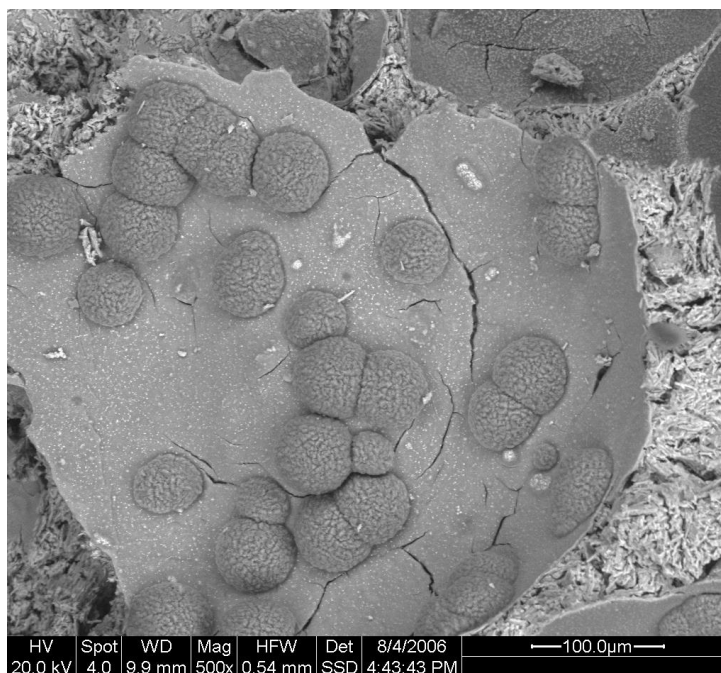


Figure (6): SEM photomicrographs of the aggregates of phillipsite crystals

X-ray Diffraction

Mineral identification by XRD indicated that there are two groups of minerals: zeolites and non-zeolites. The most abundant zeolite mineral in the samples is phillipsite (Figure 9). The analysis indicates that the main non-zeolite mineral is calcite. However, pyroxene (diopside) and olivine (forsterite) also appeared as primary rock forming minerals and calcite as secondary rock forming mineral. Tables 1 and 2 illustrate the X-ray diffraction results of all the investigated samples.

The results agree with the published data on zeolites (Breck, 1974).

Table 1. Minerals of zeolitic tuff identified by XRD

Mineral components	minerals
Zeolitic minerals	phillipsite
Non-zeolitic minerals	calcite, olive ne, pyroxene (diopside), smectite



Figure (7): SEM photomicrographs for rosiest phillipsite crystals

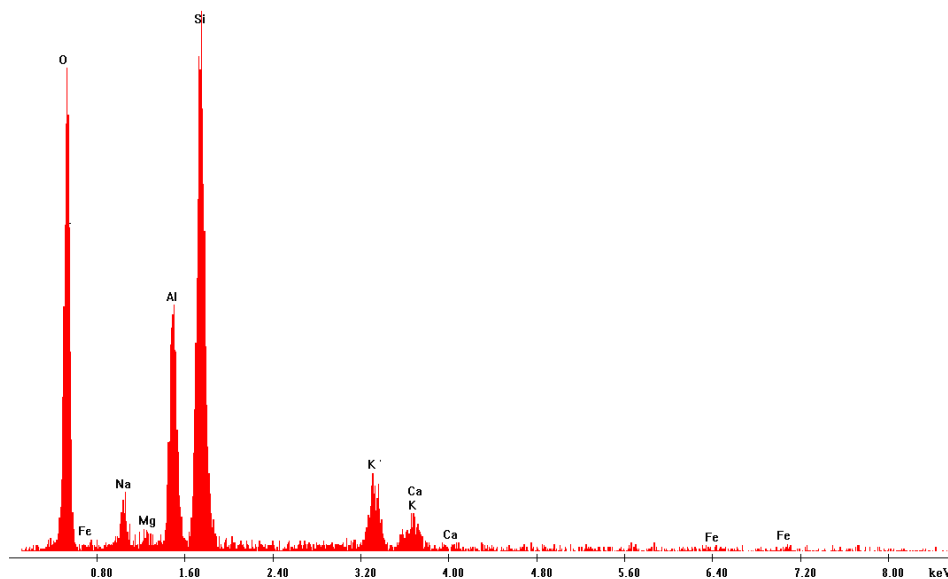


Figure (8): Energy-dispersive X-ray results of zeolitic tuff samples from Jabal Huliati Al-Gran (phillipsite crystal)

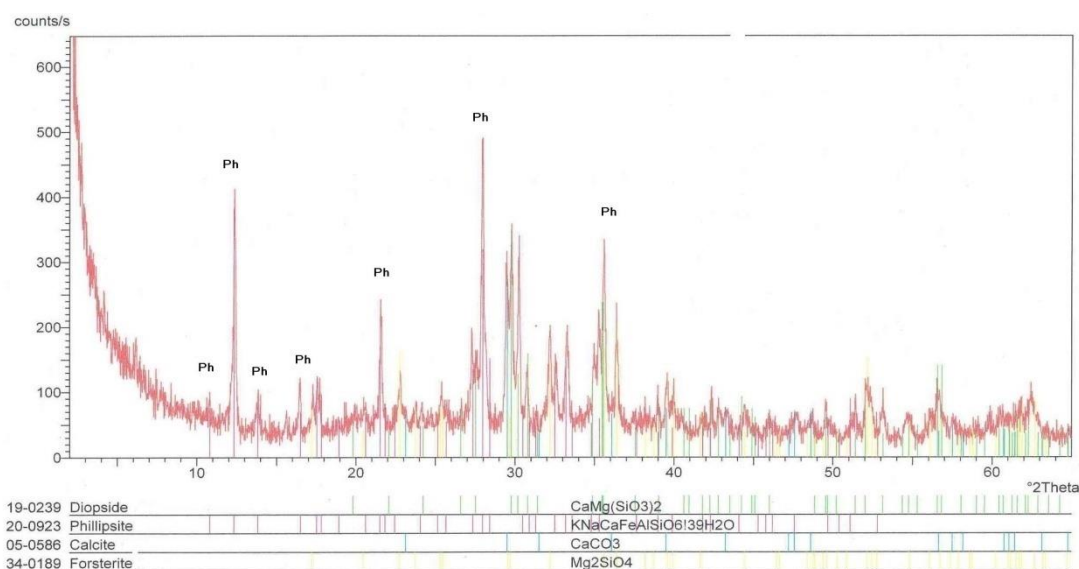


Figure (9): XRD pattern of phillipsite zeolitic tuff from the study area

Table 2. X-ray diffraction results of south Jordan

Sample	Ph	Ca	Di	Fo
G1	*	*	*	*
G2	*	*	*	*
G3	*	*	-	-
G4	*	*	*	-
G5	*	*	*	*

Ph= phillipsite Ca= calcite Di= diopside
Fo= forsterite

Thermal Analysis

DTA/TGA diagrams were used to define the exact temperature and mass of the sample where dehydration and dehydroxylation events started and ended. The main process recorded by this method is dehydration (Figure 10). The zeolites thermal behavior was studied by thermogravimetric (TGA) analyses at a temperature interval of 25-1000 °C and differential scanning calorimeter (DSC). The TGA results of the zeolitic tuff samples show a good stability under high temperature and indicate the presence of three mass losses (Fig. 10): (a) The first one takes place below 120 °C with

-0.75% mass change. This first mass loss could be attributed to sorbed water (humidity). This result agrees with DSC measurements which show absorption of energy at 120 °C (Figure 11). (b) The second mass loss is observed in the range from about 120 to 800 °C with about -5.69% mass change due to loss of deeply trapped water. (c) The sample collapse takes place at the final mass loss in the interval from 800 to 920 °C with a residual mass of 74.67 % at 1000 °C. The experiments showed that the stable new phases form at heating above 700 °C and then the following rehydration doesn't take place. This may be connected with the significant construction of the zeolite structure.

Chemical Composition

Table 3 shows the chemical composition of selected 3 zeolitic tuff samples from Jabal Huliati Al-Gran. The most abundant oxides are: SiO₂, Al₂O₃, CaO, MgO and Fe₂O₃; whereas TiO₂, MnO, K₂O and Na₂O are present only in small quantities. SiO₂ values range between 37.49 and 41.11 wt%, the average being 39.3 wt%. Similarly, Al₂O₃ contents vary between 9.32 and 10.01

wt% with an average of 9.7 wt%. The average of Fe₂O₃ analysis is 11.4 w %. Those samples with very high iron content (>10 wt%) and high MgO and CaO contents up to 9 % and 10%, respectively, are those rich in volcanic glass and calcite minerals. Those

samples with high SiO₂ and Al₂O₃ are rich in zeolites and clay minerals. The relationship between SiO₂ and Loss On Ignition (LOI) is a negative relationship. This is a good indicator that SiO₂ was lost during the alteration process.

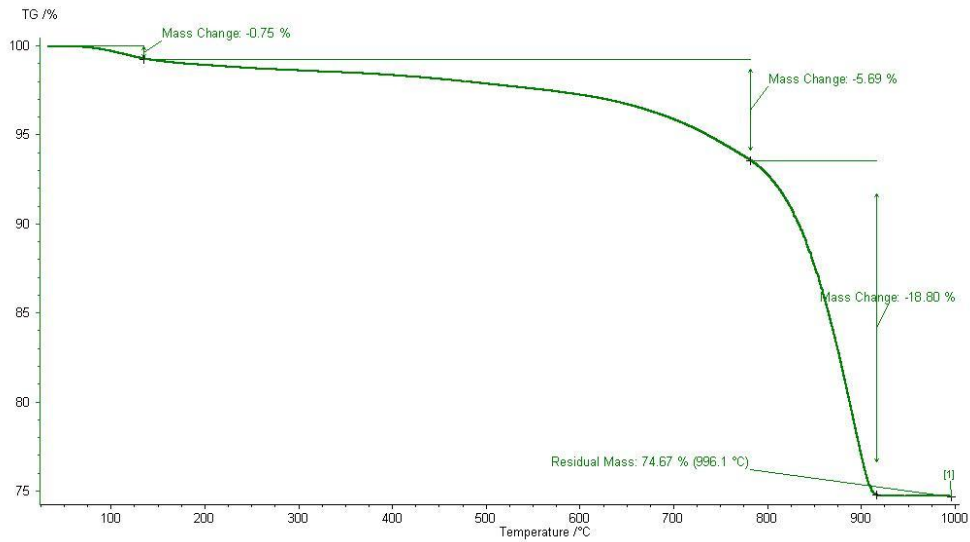


Figure (10): TGA curve of the zeolitic tuff sample from Jabal Huliat Al-Gran

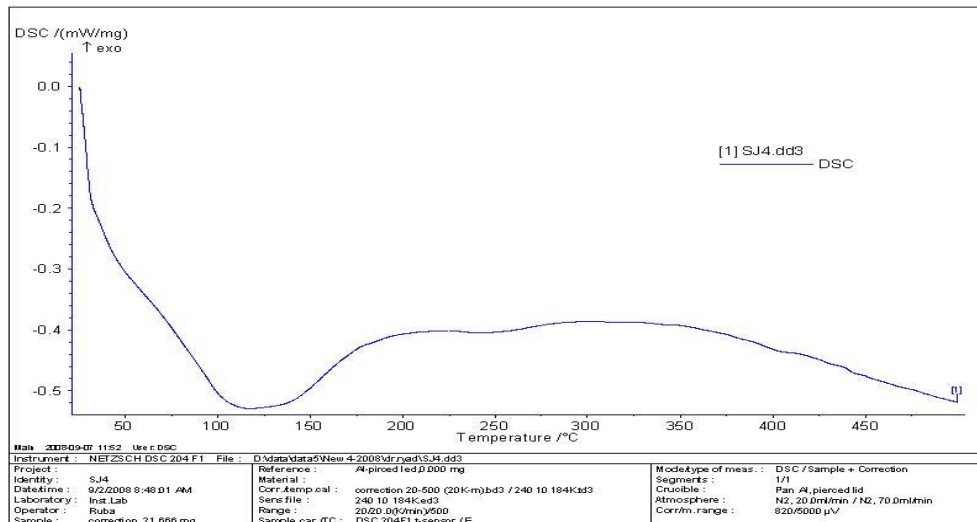


Figure (11): DSC curve of the zeolitic tuff sample from Jabal Huliat Al-Gran

Table 3. Chemical composition of the averaged zeolite sample components

Sample No.	G1	G2	G3
SiO ₂ %	42.11	39.3	37.49
TiO ₂ %	2.53	2.71	2.55
Al ₂ O ₃ %	9.88	9.32	10.01
Fe ₂ O ₃ %	11.12	11.43	11.7
MnO %	0.2	0.21	0.19
MgO %	9.29	9.11	8.39
CaO %	10.34	10.7	10.43
Na ₂ O ₃ %	2.26	2.87	2.56
K ₂ O %	3.21	3.67	2.98
LOI %	9.11	10.67	13.19
SUM %	100.05	99.99	99.49

CONCLUSIONS

- 1- The basaltic volcanism of Jabal Huliati Al- Gran is of Pliocene- Pleistocene age.
- 2- The majority of the basaltic cover in the study area originated from the Northern Huliati Al-Gran mountain.
- 3- The petrological and mineralogical identification of the volcanic tuff from Huliati Al- Gran is composed of a phillipsite-cemented palagonite ash tuff unit. The results indicated that there are two groups of minerals: primary rock forming minerals such as

olivine and pyroxene, and secondary rock forming minerals such as zeolites (phillipsite and chabazite), smectite and calcite.

- 4- Geochemical studies show that the studied samples are highly weathered to secondary rock forming minerals (Zeolites).
- 5- Thermal analysis indicated that Huliati Al-Gran zeolitic tuff has high structure stability and high percentage of water which enable them to be used widely in industry as catalysts and pollution controllers.

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