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Mineralogy and Authigenesis of Zeolitic Tuff from Tall-Juhira and Tall Amir, South Jordan

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Abstract

Tall Amir and Tall Juhira are two important volcanoes located in southern Jordan. Huge quantities of zeolitic tuff deposits are existed within basaltic rocks. These two localities haven't been investigated nor evaluated for their mineralogical and zeolitic content. Zeolitic tuff from south Jordan is composed mainly of three components: Volcanic glass, primary rock forming minerals and secondary rock forming minerals.

Zeolitic tuff from Tall Juhira (ZTJ) are characterized by highly weathered red to brown color, and friable tuff. The main zeolitic tuff minerals in ZTJ are phillipsite and chabazite.

Zeolitic tuff from Tall Amir (ZTA) is characterized by gray color and well-cemented tuff. The main zeolitic tuff minerals are phillipsite, chabazite and analcime.

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Keywords: Zeolitic tuff; Tall-Juhira; Tall Amir; Phillipsite; Chabazite; Analcime.

1. Introduction

Zeolitic tuff associated with basaltic rocks in Jordan are exposed in different localities include northeast, central and south of Jordan, Figure (1) shows two important locations of basaltic volcano. The first one is Tall Juhira with latitude of (30° 38' 47") and longitude of (35° 49' 37") with a height of about (1355 m). It is one of the most important deposits of zeolitic tuff in the south of Jordan. The second one is Tall Amir with a latitude of (30° 33' 05") and longitude of (35° 47' 58") with a height of about (1049 m).

The study area is characterized by rainy period which is short in the studied volcanoes areas (December to March) with average annual precipitation of about 100 mm, the rest of the year is warm and dry. Occasional Snow falls mainly in the highlands, and may reach 70 cm in thickness. The maximum recorded temperature is 39 C° in July.

2. Regional Geology

Basalt in the studied areas is of Neogene age. It comprises porphyritic, fine grained rocks. The previous petrological, geochemical and geostatistical studies that dealt with the basalt from the study area demonstrates that they are sodic alkalic basalts that belong to the alkali olivine basalt series, and are considered as nepheline basanite (Ibrahim, 1987).

According to Ibrahim (1987) the essential minerals in the basaltic samples are pyroxene, plagioclase and olivine with variable amounts of opaques and nepheline. Apatite is the most abundant accessory mineral.



Fig. (1). Location map of the studied basaltic volcano.

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Uneiza volcano is type localities for the basalt along the Dead Sea Rift in southern Jordan (1143m high). It comprises one of the symmetrical volcanic centers with basaltic flows separated by zones of pyroclastic deposits. The rocks of the volcano are 110 m thick of lapilli, ash, welded tuff, and basaltic flow. The lithics are angular to rounded and consist of carbonates, phosphates, shale, and chert. The studied cross section include two types of ejecta: the first one is at the bottom and belong to the Aritayn type which consists of reddish brown well bedded, well sorted, well cemented, fining upward pyroclastic with small bombs, and Zeolites in this ejecta occur as cementing material. And the second type is the Hassan type, which consists of violet to black, poorly sorted, poorly cemented, angular to sub angular pyroclastics. The total thickness of the Aritayn type is 18 m in Jordan, while the Hassan type thickness is only 3 meters thick. Figure (2) is a columnar section of Jabal Uneiza volcano after (Ghrir, 1998).

	Location	Thickness	Horizon	Lithology	Description
IIncira Volcano		20	Upper Zone Sideromelane Zone		Agglomerated, bad sorted bed cemented, dominated by basaltic to scorasious bombs and show variation in color form violet to black, with carbonate.
	Uneiza Volcano		Middle zone Palagonite		Normal grading ashes, well sorted, well cemented, laminated Normal grading lapilli, well sorted, well cemented with carbonate and silicsous lithic, dominated by small rounded bombes at the lower part.
					Ashes, well sorted well cemented with carbonate Normal grading lapilli, well sorted, well cemented, brownish color, carbonate and shale lithic. Ashes, well sorted, well cemented, laminated, brownish color.
			Lower Zone Zeolite Zone		Normal grading lapilli, well sorted, well cemented, with few small bombs.
					Medium to coarse lapilli, bad sorted, well cemented, brownish red color, dominated by bombs. Fine to coarse lapilli, bad sorted, well cemented with carbonate lithic, dominated by small bombs , reddish brown
					color highly zeolite content.
		0			

Fig. (2) Columnar section of Jabal Uneiza volcano after (Ghrir, 1998).

3. Materials and Methods

Ten fresh representative channel samples were collected from the two volcanic centers and zeolitic tuff outcrop, five samples of each location.

Thin section petrography was carried out by using impregnation method. Ten thin sections of zeolitic tuff from the two locations were prepared and examined under the polarizing microscope.

The samples were investigated using scanning electron microscope (SEM) (Quanta 600 F, FEI) combined with Energy-dispersive X-ray analysis (EDX) mapping (Genesis 4000, EDAX) available in BGR, Hanover, Germany. EDX (spot analysis) was carried out during the progress of SEM studies. With SEM/EDX analyses technique, samples were investigated for their physical properties including size, shape, and surface morphology. EDX provides information on the chemistry of the individual particles.

X-ray Diffraction Analysis (XRD) for random preparation samples was done using Phillips X-ray Diffractometer. Random preparations for X-ray diffraction analyses were also made for zeolitic fractions of the size range between (1) mm and (0.3) mm.

4. Results

4.1. Transmitted polarizing microscope results

Thin sections investigation shows that the tuffaceous basaltic samples are composed of four major components: 1. Vesicles

- 2. Volcanic glass and Palagonite
- 3. Major rock forming primary minerals (olivine, nepheline, pyroxene, plagioclase)
- 4. Secondary weathering product minerals (zeolites, iron oxides, clay minerals, and calcite)

The volcanic tuff can be divided into two components (pyroginic and authigenic minerals) according to the mineral formation phases. The term pyroginic refers to the host mineral phase (major rock forming minerals), while the term authigenic refers to the alteration product (secondary product minerals).

The break down of rock-forming primary minerals during weathering transfers them into secondary minerals as alteration products. Willson (2004) has described the weathering of pyroginic minerals and their alteration product. He found that olivine, plagioclase, and pyroxene break down during weathering to clay minerals, Fe oxides, and Ca, Na, K aluminosilicate rich minerals.

The studied thin sections show that most of the samples are highly-altered tuffaceous volcanic basalt. The weathering of volcanic rocks from all localities is indicated by number of presented phases. Thin sections investigation shows that the secondary weathered products are zeolites (phillipsite, chabazite, and analcime) and non zeolites such as smectite, calcite, and gypsum. The detailed results of thin section studies for both primary and secondary minerals are as follow:

4.1.1. Vesicles (V)

The results of studied samples indicate a typical vesicular texture of different degrees. These vesicles are mainly empty or filled with a secondary filling material. These vesicles are circular, subcircular and irregular in shape (Figure 3).

4.1.2. Volcanic Glass (Vg) and Palagonite (Pl)

Low-temperature alteration of basaltic glass produces palagonite. The world palagonite was used to describe the altered basaltic glass of the hyloclastics from palagonia in the Hyblean Mounts, Sicily (Honnorez, 1981). Palagonite is present in most of the studied thin sections with variable colors that range from dark brown, yellow brown to deep red, depending on the degree of alteration (palagonitization). Palagonite occurs as microphenocrysts in the groundmass of all thin sections. Lath shape euhedral tabular crystals with zeolitic coating are common (Figure 3). Under the binocular microscope, palagonite is characterized by its vitreous, wax like or resinous luster with a conchoidal fracture.

The studied thin sections show two types of volcanic glass. These are fresh volcanic glass and weathered volcanic glass (palagonite). Palagonite is not stable and tends to crystallize to zeolites and chlorite as alteration products. The alteration of palagonite (palagonitization) gives the general chemical composition of SiO₂, Al₂O₃, Fe₂O₃, FeO, MgO, and H₂O (Kerr, 1977). The studied altered tuff shows all samples from Tall Juhira are characterized by the presence of palagonitic glass with different degrees of alteration while four samples from Tall Amir shows palagonitization.



Fig. (3) vesicles from south Jordan zeolitic tiff (Tall Amir)

4.1.3. Major Rock Forming Primary Minerals

a- Olivine (Ol)

Olivine and its alteration product iddingsite (Id) are the most abundant microphenocrysts in most of the slides. Olivine is usually colorless and is highly fractured in the plain polarized light. The fresh crystals show olive green to pink interference colors. The crystals range in length from 0.3 to 2 mm. Olivine is altered to iddingsite (Id). Figure 4 shows a microphotograph from Tall Amir that is highly-altered olivine crystal to iddingsite. The iddingsitization is seen to surround the margins and the innermost parts of the crystal. Some crystals show corroded outlines and embayment.

Olivine usually is destroyed or replaced during the early stage of weathering. Olivine is altered by deuteric or hydrothermal process to a mixture of hydrous phyllosilicates and Fe-oxide minerals. In the latter case, the most common product is iddingsite, which may be optically homogeneous and crystallographically oriented with respect to the parent olivine (Wilson, 2004).

The transformation from olivine to iddingsite was studied in detail by Eggleton (1984), using transmission electron microscopy of ion-beam thinned specimens. A two-stage process was proposed. In the first stage, the olivine breaks down into thin lamellae consisting of a metastable hexagonal phase and elongated parallel to the olivine c axis. This transformation opens up solution channels which become infilled with lath-like crystals of saponite. In the second stage, water migrates more freely through the solution channels and permitting further growth of the smectite and goethite nuclei formed during early alteration and largely, but not entirely. In this instance, alteration was undoubtedly due to deuteric / hydrothermal activity, although weathering was considered to result in similar mineral assemblages. This point was amplified in a later study on the weathering of olivine in basalt to iddingsite by Smith et al, (1987). Three different basalts were examined. In each, the process of iddingsitization appears to have commenced before weathering, but progresses to completion as a result of later weathering. Iddingsite formation again involves etching along lamellar zones parallel to (001) and formation of smectite and oriented goethite within these zones. An important finding, however, is that some elements such as Al and Na, have been introduced from outside the weathering olivine crystal, showing that the process is not truly isochemical. In fact, in the later stages of decomposition, dioctahedral smectite and halloysite are associated with the weathered olivine. The initial stages of the alteration of olivine were explored in further detail by Banfield et al, (1990). It was founded that in altered basaltic andesites, the olivine consisted of fine intergrowths of forsterite-rich olivine and laihunite, an oxidized favalitic phase where structural ferric iron is balanced by structural vacancies resulting in a distorted olivine structure. Where the intergrowths are widely spaced, the laihunite act as a barrier to weathering, resulting in the preferential dissolution and etching out of the forsterite to yield textures very similar to those reported by Eggleton (1984) and Smith et al, (1987). The etched out channels are first filled with semi-oriented aggregates of saponitic clay and subsequently with aggregates of oriented hematite crystals.

b- Plagioclase (Pla)

The second important rock forming mineral in the studied samples and the most abundant after olivine is plagioclase. In thin sections, plagioclase is found as phenocrysts or small laths in the groundmass. The crystals shape is euhedral to subhedral. The phenocrysts and lathes show albite twinning. In all thin section, plagioclase shows a highly strong alteration with partly or completely damaged crystals. Figure 5 shows lath shaped slightly altered plagioclase crystals which are dominated in most of the studied thin sections.

c- Pyroxene (Py)

High-Ca pyroxene diopside and augite are the most abundant clinopyroxenes in the studied thin sections. In thin sections clinopyroxene are colorless, pale green to bright green, and subhedral crystals. Figure 5 shows augite with plagioclase crystals as groundmass in most of the studied localities.

Orthopyroxenes are not abundant and are observed in restricted samples. Pyroxene have been found to weather to hydrous layer silicates in a similar way to that described for olivine (Willson, 2004).

d- Nepheline

The most abundant feldspathoidal mineral in all thin sections is nepheline. In thin sections, it appears colorless to turbid, euhedral to anhedral crystals. Nepheline crystals in most of slides are altered and not clear in the groundmass of basaltic tuff. The alteration product of nepheline is zeolites (Kerr, 1977).



Fig. (4) Fe-oxides and iddingsite and augite with plagioclase crystals as groundmass from Tall Amir SJ.



Fig. (5) shows lath shaped slightly altered plagioclase crystals which are dominated in most of the studied thin sections.

4.1.4. Secondary Mineral Products (SM)

4.1.4.1 Zeolites

a-Phillipsite (Ph)

All samples from Tall Juhira south Jordan show phillipsitic crystals growth. It occur mainly as colorless, radial, fan shape crystal that is forming a thin rim of phillipsite crystals. Phillipsite is the most abundant zeolitic mineral in all of the studied samples. It grows may be directly as the earliest phase in the walls of palagonite vesicles.

Figure 6 from Tall Juhira shows that phillipsite occurs as a rim of crystals growing directly on palagonite. Figure 7 from Tall Amir shows phillipsite growth as the first phase growth as a rim that shows a radial (fan like) shape growth of phillipsitic crystals with an assemblages of chabazite crystals while other plates show spherulitic growth of phillipsite crystals.

c- Chabazite (Ch)

Chabazite was reported for the first time in Jordan by Dwairi (1987) in Aritayn. Ibrahim (1993) described chabazite crystals from Jabal Aritayn as strongly zoned, elongated rhombohedra crystals with a complex penetration twinning. In all of the investigated sites, chabazite appears as colorless rhombohedra crystals with twinning and zoning.

Figure 7 shows that chabazite crystals grow as a second phase preceded phillipsite as indicated in samples from Tall Amir. Figure 8 shows a sugar like growth of chabazite crystals from Tall Juhira. All samples from this location show chabazite crystals.

4.1.4.2 Non Zeolitic Minerals

a - Clay minerals (Smectite (Sm))

Smectite form the earliest alteration product of the authigenic minerals. It appears as colorless, cloudy rim fringing palagonite granules and/or encrusting the vesicle walls with minute fringes (Figure 9) in most of the samples. This rim is circular in shape; and locks to form a flaky habit. It is absent in three samples from Tall Juhira, depending on the type and the degree of weathering. The most abundant smectite mineral in all samples is montmorillonite.

4.2 Scanning Electron Microscope and Energy-Dispersive X-ray Results.

Scanning electron microscopes (SEM) was carried out combined with energy-dispersive X-ray analysis (EDX) for all samples from Tall Juhira and Tall Amir. SEM/EDX analyses show that there are different zeolitic minerals included within the zeolitic tuff such as phillipsite, chabazite and analcime.

a- Phillipsite

Phillipsite is the most abundant zeolitic mineral that appears under the SEM. It occurs as spherulitic radiating prismatic crystals. The spherulites are about 100 μ m to have zoning, and range in length from 100 μ m to 200 μ m and in width from 10 μ m to 5 μ m with a dome cap at the end of the prism



Fig. (6). Sample from Tall Juhira show that phillipsite occurs as a rim of crystals growing directly on palagonite followed by the growth of chabazite phase.



Fig. (7). Photograph shows a rim of phillipsite growth as a radial



Fig. (8). Photograph show a sugar like growth of chabazite crystals as indicated in samples from Tall Juhira 150µm in diameter while the prismatic crystals commonly (fan like) shape growth of phillipsitic crystals from Tall Amir.



Fig. (9). Photograph shows a rim of clay minerals (smectite).

Figure 10 shows a group of growing prismatic phillipsitic crystals radiating from a growth center with a diameter range between 50 μ m and 100 μ m from Tall Juhira. Figure 11 shows two generations of phillipsite crystals from Tall Amir.

EDX results for phillipsite crystals are illustrated in Figures (12 and 13). Figure 12 from Tall Juhira shows that the chemical composition of phillipsitic crystals (K, Na, Ca) (Si, Al)₈ O₁₆ has variable amounts of Na, K, and Ca. Figure 13 shows EDX results for phillipsite crystals from Tall Amir shows a high content of Na, K, and Ca. Phillipsite from Tall Juhira show high content of Ca and K and small amounts of Na as indicated in figure 12.

b- Chabazite

Dwairi (1987) described chabazite from Aritayn as wall rim crystals. Ibrahim (1993) has described also chabazite from Jabal Tarbush as rhombohedral crystals with dimensions range between 10-80 μ m.

Chabazite is the second abundant zeolitic mineral after phillipsite in all studied localities. Chabazite crystals appear as a group of rhombohedral crystals with simple and complex penetration twinning. Crystals from the study areas range in dimensions from several microns to 15 μ m. Chabazite from Tall Juhira, as in Figure 14, shows a complex penetration twinning with dimensions range between 15-20 μ m. Both chabazite and phillipsite occur together as illustrated in Figure 14. Moreover, aggregates of chabazite crystals from Tall Amir grow directly on palagonite walls, as in figure 15.

EDX analysis for chabazite crystals for the two sites indicates a high content of Ca as illustrated in Figures (16 and 17). Chabazite from the two sites has a possible chemical composition similar to the theoretical chabazite of $CaAl_2Si_4O_{12}.6H_2O$.

d- Analcime

Analcime is the third zeolitic mineral found in the study area. It is restricted to Tall Amir locality. Analcime under the SEM appears as isolated euhedral crystals (rhombdodecahedron form). Figure 18 shows isolated

euhedral crystals of analcime from Tall Amir. EDX data for analcime from Tall Amir showed high content of Na as indicated in figure 19. The theoretical chemical composition of analcime is $NaAlSi_2O_8.H_2O$.

E- Smectite

It is one of the most important non zeolitic secondary minerals which are associated with phillipsite and chabazite. It is the main alteration product of the basaltic volcanic glass; and is developed in the early stage of alteration. Smectite under the SEM appears as circular to semi circular aggregates forming colloform structure. The circles have a radius of less than 30 µm. Figure 20 shows smectite circular growth with a cornflakes appearance.



Fig. (10) SEM photo shows a prismatic phillipsite crystals from Tall Juhira.



Fig. (11) SEM photo shows two generations of phillipsite crystals from Tall Amir



Fig. (12) Energy-dispersive X-ray results of zeolitic tuff (phillipsite) samples from Tall Juhira



Fig. (13) Energy-dispersive X-ray results of zeolitic tuff (phillipsite) samples Tall Amir.

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Fig. (14) SEM photo showing Simple twining of chabazite crystals and phillipsite growth from Tall Juhira



Fig. (15) SEM photo showing assemblages of chabazite from Tall Amir



Fig. (16) Energy-dispersive X-ray results of zeolitic tuff (chabazite) for samples from Tall Juhira



Fig. (17) Energy-dispersive X-ray results of zeolitic tuff (chabazite) the sample from Tall Amir.



Fig. (18) SEM photo showing assemblages of analcime from Tall Amir.



Fig. (19) Energy-dispersive X-ray results of zeolitic tuff (analcime) for sample from Tall Amir.



Fig. (20) SEM photo for the smectite colloform structure from Tall Juhira.

4.3 X - Ray Diffraction Results

Figures 21 and 22 are the X-ray diffraction patterns of the zeolitic tuff samples, which indicated the presence of two main groups of minerals zeolites and non-zeolites. Table (1) illustrates the X-ray diffraction results of all the investigated sites. Table (2) gives the detailed results of the studied samples. The results are in agreement with the published data on zeolites (Breck, 1974)

The X-ray diffraction patterns show that zeolitic tuff samples contain different zeolitic minerals such as phillipsite and chabazite (Table 1). The most abundant mineral is phillipsite; and is present in all of the studied samples while chabazite is present as the second abundant mineral.

Table (1) Minerals of zeolitic tuff identified by XRD

Mineral components	minerals			
Zeolitic minerals	phillipsite, chabazite, analcime			
Non zeolitic minerals	calcite, olivine, plagioclase, pyroxene (augite and diopside), smectite, gypsum, hematite			

S.No	Ph	Ch	An	Не	Са	F	Di	Fo	Sm
ZTA1	*	*	-	-	*	-	*	*	-
ZTA2	*	*	*	-	*	-	*	*	-
ZTA3	*	*	-	*	*	*	-	-	-
ZTA4	*	-	*	*	*	-	*	-	*
ZTJ1	*	*	-	-	*	-	*	*	*
ZTJ2	*	*	-	*	*	*	-	-	-
ZTJ3	*	-	-	*	*	-	*	-	-
ZTJ4	*	*	-	-	*	-	*	-	*

Table (2) X-ray diffraction results of Tall Juhira and Tall Amir, south Jordan.

Ph= phillipsite Ch= chabazite An= analcime He= Hematite Ca= calcite

F= feldspar Di= diopside Fo= forstrite Sm= Smectite



Fig. (21) X R D pattern of the zeolitic tuff sample from Tall Juhira.



Fig. (22) XRD pattern of the zeolitic tuff sample Tall Amir.

5. Discussion

SEM/EDX, XRD and TS results have indicated that the studied tuffaceous basaltic samples are highly altered volcanic glass. The studied samples are composed of olivine, plagioclase, pyroxene, nepheline and volcanic glass. Olivine is altered to iddingsite. Plagioclase and pyroxene are altered to aluminosilicate and Fe, Mg gels. Nepheline is altered to zeolite. Zeolitic tuff is a weathering product as a result of the reaction of volcanic glass with invading percolating waters. Zeolites are most readily found in alkaline environments (pH>8) because silica is more soluble under these conditions, and thus the supply of most essential reactant is greater. Furthermore, because Ca, K and Na are essential for zeolite structure formation, zeolites tend to form in an environment where these ions are abundant (Hawkins, 1984).

In Jordan, the formation of zeolitic tuff as a result of the alteration of the basaltic tuff was studied by many authors Such as (Dwairi 1987 and 1991) who described the zeolitic deposits in Aritayn area. He divided the zeolitic tuff deposits into three types depending on their degree of zeolitization as follows:

- a. Least zeolitized tuff (violet zeolitic tuff).
- b. Moderately zeolitic tuff (brownish zeolitic tuff), and
- c. Highly zeolitic tuff (reddish zeolitic tuff).

The formation sequence of Jordanian phillipsite in Aritayn area was explained by Dwairi, 1987 and 1991 as a reaction process of basaltic glass with alkaline water according to the following steps:

- d. The reaction between volcanic glass and percolating alkaline water has lead to the formation of palagonite with a thin film of intergranular phillipsite.
- e. Palagonite has reacted with Mg-rich percolating solutions to form the Mg-clay.
- f. Mg-clay then was altered to aluminosilicate gel.
- g. The reaction of aluminosilicate gel with Na+ and K+ rich percolating water has led to the formation of insitu phillipsite.

Ibrahim (1993) has explained the formation of authigenic minerals in Aritayn according to following paragenesis: [Fresh sideromelane \rightarrow palagonite \rightarrow smectite \rightarrow faujasite

 \rightarrow phillipsite \rightarrow chabazite \rightarrow natrolite \rightarrow analcime \rightarrow calcite]. Hay and Lijima (1968b) reported the following sequence of authigenic minerals:

[Phillipsite \rightarrow chabazite \rightarrow thomsonlite \rightarrow gonnardite \rightarrow natrolite \rightarrow analcime or faujasite \rightarrow montmorillonite \rightarrow calcite \rightarrow gypsum].

The SEM/EDX and petrographic results aided by X-ray diffraction analysis, the order of paragenesis of the principle authigenic minerals in the different localities are indicated as follow:

[Fresh sideromelane \rightarrow palagonite \rightarrow smectite (montmorillonite) \rightarrow phillipsite \rightarrow chabazite \rightarrow analcime \rightarrow calcite \rightarrow gypsum].

The above order is similar to the paragenesis of Ibrahim (1993) and Hay and Lijima (1968b). Natrolite was not identified during the current work. Faujasite is restricted to Northeast Jordan, while analcime appears only in South Jordan. Gypsum is shown in South Jordan sequence.

6. Conclusion

- 1. Tall Juhira and Tall Amir are two important Jordanian zeolitic tuffs outcropping in southern Jordan.
- The Jordanian zeolitic tuff is highly weathered and is altered mainly to zeolites (chabazite, phillipsite, and analcime), clay minerals, calcite, gypsum, and hematite.

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