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MINERALOGY AND PETROGRAPHY OF NEW OCCURENCES DEPOSITS OF THE ZEOLITIC TUFF IN NORTHEAST JORDAN

K. Tarawneh
Natural Resources Authority, Geology Directorate, P.O.Box 7. Aman, Jordan, e-mail: Tarrawnehkh@hotmail.com

ABSTRACT. The occurrences deposits of the zeolitic tuff were studied in four areas through detailed geological mapping at a scale 1:50.000 in northeast Jordan and through exploration project. These deposits covered large areas and characterized by rich content, lateral and vertical homogenous distribution of the zeolite minerals. The zeolites are an abundant constituent in these deposits, which form more than 50% of the rock. A detailed field investigation was carried out along systematic horizontal and vertical sampling and subsurface samples from boreholes and trenches. A detailed petrographic, mineralogical and geochemical investigations including XRD, XRF, optical, electron microscopy, binocular microscope, polarizing microscope and SEM were carried out on the samples to understand the nature of the zeolite minerals of these deposits. The new zeolitic tuff deposits are of commercial value due to the high content of the zeolite minerals, contain large grain size zeolite minerals, relatively poorly lithified and porous. These properties are all favourable for successful beneficiation. Experimental investigations on the zeolitic tuff emphasized the importance of the Jordanian zeolites for use in wastewater treatment plants and as a soil conditioner and as slow- release fertilizer.

МИНЕРАЛОГИЯ И ПЕТРОГРАФИЯ НА НОВИТЕ НАХОДИЩА НА ЗЕОЛИТНИ ТУФИ В СЕВЕРОИЗТОЧНА ЙОРДАНИЯ

Х. Тараунех
Национална служба по полезни изкопаеми, п.к. 7, Аман, Йордания, e-mail: Tarrawnehkh@hotmail.com

РЕЗЮМЕ. Находищата на зеолитни туфи са проучени в четири площи в североизточна Йордания с детайлно геоложко картиране в мащаб 1:50.000 в и проект за проучване. Тези находища са разположени на големи площи и се характеризират с високо съдържание на зеолитните минерали, равномерно разпределени във вертикална и хоризонтална посока. Зеолитите са главен скалообразуващ минерал, който формира повече от 50 % от основната скала. Проведено е детайлно полево проучване посредством систематично хоризонтално и вертикално опробване, като голям брой от пробите са взети от сондажи и канави. На пробите са извършени детайлни петрографски, минераложки и геохимични изследвания, включващи XRD, XRF, оптически методи, микроскопия с поляризационен микроскоп и спектрален емисионен анализ с цел изясняване на характеристиката е на зеолитните минерали от тези находища. Тези нови находища на зеолитни туфи имат икономическо значение, поради високото съдържание на зеолитни минерали, съдържанието на зеолитни минерали с голям размер на зърната, относително ниската литификация и порестост. Всички тези свойства са благоприятни за успешното обогатяване на суровината. Експерименталните изследвания на зеолитни туфи подчертават значението на йорданските зеолити за използване в пречиствателните станции за отпадъчни води и като торове за бавно подобряване свойствата на почвата.

Introduction

The new occurrences of the zeolitic tuff deposits are belong to the Cenozoic continental basaltic rocks exposed in northeast Jordan which are the northern extension of the North Arabian Volcanic Province. This province covers a total area of more than 46.000 km^2 (from Syria to Saudi Arabia) of which 11.000 km^2 are only in Jordan. The province is underlain by the Azraq-Sirhan Graben that is parallel to the axis of the Red Sea and is truncated at the Dead Sea-Gulf of Aqaba Transform Fault.

Detailed geological mapping of the northeast Jordan was carried out by the Natural Resources Authority since 1988, which allowed to produce several 1:50,000 geological maps. Ibrahim (1993) studied in detail the basaltic province, redefined and subdivided the exposed volcanics of the Harrat Ash Shaam Basaltic Super-Group into five groups: Wisad, Safawi, Asfar, Rimah and Bishriyya.

Based on new K-Ar dating of the basalt Tarawneh *et al.* (2000), subdivided the Harrat Ash Shaam Basaltic Super- Group into three major phases. The first phase is of Oligocene age 26.0-21.0 Ma. The second phase is of late Miocene (12-8Ma) and the third phase is mostly of Pliocene – Quaternary (6-<0.5Ma).

Geological Setting of the Zeolite Depoists

Phillipsite tuff was discovered by Dwairi (1987) in Jabal Aritayn, whereas, the economic zeolite deposits in the other localities in the Badia region were discovered by Ibrahim, (1996) including Jabal Aritayn, Tell Rimah, Tell Hassan, Tulul Al Ashaqif which are belong to the Aritayn Volcaniclastic Formation with variable thickness from few meters up to 100 m. The new occurrences of the zeolite and zeolitic tuff were indicated also in Tlull Hmelan, Tlull Hasnah,Jabal Hannoun and are belong to the Tlull Ash Shahba (Al Ashagef) area (Tarawneh et al., 2002). These deposits litholgically and stratigraphically are belong to the Aritayn Volcaniclasitcs Formation (AVF) which is part of the Rimah Group (RG).

The AVF is part of composite cider cones and stratovolcanic centers type and is composed mostly of pyroclasitc materials interbedded with thin layers of lava flows. The AVF consists of stratified, sorted, poorly cemented air-fall tuff and agglomerate intercalated. The pyroclasitcs consist of fine-grained ash, angular to subangular and spherical lapilli, volcanics bombs, blocks and lithic fragments and mantle-derived xenolith. Ibrahim (1995) subdivided the AVF into three distinctive diagentic zones with respect to degree of alteration of sideromelan or basaltic glass. The upper zone contains fresh sideromelan (8-40m thick). It consist mainly of welded agglomerates, weldded labilli tuff alternating with tephra; The middle zone is characterized by palagonitization of sideromelan (10-20m thick) and comprises palagonitized tuff composed of badly sorted labilli and scoria blocks and it is characterised by variable colours from dark brown to reddish brown. The lower zone (6-40 m thick) is the zone of zeolitization, where the tuff granules are cemented by a colorless to white coating composed of zeolites and calcite (Ibrahim, 1996). Field evidences indicate that both vertical and lateral zoning in the distribution of zeolite minerals have been established. There is no significant difference in geological setting among the different new localities in the study area.

The zeolite minerals are formed in pore spaces among the glass shards as well as in the vesicles and bubbles of the volcanic tuff. From the top to the bottom direction the quantity of the zeolite reach up to 60 %.

Analytical Methods

More than 100 samples from boreholes and outcrops were examined meanly by means of X-ray diffraction, XRF and ICP analysis. The mode of occurrences of the authoginic minerals was observed by petrographic microscope and SEM.

Results and Discussion

Detailed field investigation of the Aritayn Formation by Ibrahim (1996b) indicate the presence of the vertical zonation more or less similar to these described in Kako Crater, Hawaii, by Hay and Iijima (1968). According Ibrahim (1996) the zonation is defined with respect to the degree of alteration of sideromelane to a reddish-brown colored palagonite, from a surface zone "Zone 1" contains a relatively fresh sideromelane to a zeolitic zone "Zone 3", with an intermediate zone of palagonite which is almost free of zeolite "Zone 2". At outcrop the zones can be recognized by their distinctive weathering colors. In detailed, Zone 1 consists mainly of massive and thick layers of welded agglomerates, welded lapilli tuff alternated with tephra laminae, all of which contain nearly fresh sideromelane and sometimes cemented by carbonate. It is distinguished by black to light gray color and is variable in thickness from 10 m up to 40 m due to local variation in permeability. Zone 2 is 10 m to 20 m thick, comprises palagonitized tuff composed of badly sorted lapilli and sometimes scoria blocks, and is characterized by dark brown to reddish brown colors. In Zone 3, the zeolites vary from a small percent up to 60% of the total mineral phases in the rock, occur chiefly in form of cement combining the fore-mentioned clasts and also they line or fill vesicles. In some examples, zeolites were also found replacing glass fragments.

It displays distinctive yellowish light brown color. The highly zeolitized areas contain soft and friable highly altered lapilli clasts cemented by a thick coating of zeolite and calcite. In a few cases, zeolite bearing lenses and/or bands follow the joints system in Zone 2. The exposed thickness of the zeolitic zone is between 6 m and 20 m. The contact between zones are sharp and roughly follow the topography and cuts across stratification. Diagenesis involves palagonitization of sideromelane and the formation of authigenic minerals including zeolites and calcite. The amount of the former is generally proportional to the amount of palagonite in the tuff, a fact emphasized by previous studies (i.e., Hay and Iijima, 1968).The detailed mineralogy of the zones and further classification to sub-zones are described in this paper.

1. Volcanic Tephra

The volcanic tephra comprises massive, poorly cemented lapilli vitric tuff to coarse vitric ash tuff. The cementing material consist essentially of zeolite and calcite. Clasts are usually sub-angular, and less than 5 mm in grain size with poor packing. In addition to fresh and palagonitized sideromelane clasts, the tuff contains lesser amounts of crystal shards and lithic clasts. Crystal shards are made mainly of olivine, fewer amounts of ortho- and clinopyroxene, and minor amounts of spinel. The lithic clasts consist of the following lithologies: Vesicular, brown to dark brown, microcrystalline, olivine phyric basalt, and pyroxene olivine phyric basalt; upper crustal inclusions including sandstone, limestone, quartzite, argillite, chert and phosphorite and ultramafic xenoliths including all the spectrum of both the (spinel) peridotite and (spinel) pyroxenite, in addition to gamet pyroxenite and Pyroxenite (enstatite) (Tarawneh and Abu Jassar, 1994).

2. Sideromelane

It comprises greenish light brown, hypohyaline, texturally uniform and smooth groundmass with fresh olivine phenocrysts or needles. pereletic cracks are exploited by dark brown to black staining. Microlites and crystallites of pyroxene and plagioclase are rare (Table 1). Vesicles are mostly rounded, but with different sizes and coated by calcite.

Table 1.
Constituent proportions of the fresh glass in the Aritayn Volcaniclastic Formation

Component	Vol. %	Component	Vol. %
Olivine phenocrysts Olivine needles	15 - 20	Pyroxene microlites Opaque	2 - 5
Plagioclase microlites	5 - 10	Sideromelane	2 - 5
	2 - 5		65 - 71

3. Palagonite

It is made of a groundmass of reddish brown to yellowish brown and golden red hydrated sideromelane with distinctive hydration polygonal cracks. The palagonte occurs either as smooth or mottled consists of tiny (less than 1 mm) massive, yellow-brown, isotropic ooidal spherulites. The palagonite granules and the vesicles inside always exhibit a darker colored mantle zone of palagonite, named by Dwairi (1987) as rim zone palagonite. Authigenic minerals usually coat both the granules and the vesicles. The chemical composition of palagonite, is rather variable and reflects the degree of the palagonitization. It was noticed by many authors that Fe and Ti content in the palagonite is proportional to the degree of the palagonitization of the sideromelane.

4. Faujasite

Faujasite is discovered by Ibrahim and Hall (1995). It occurs in colorless, equant, isotropic, isolated and aggregated crystals. It always tends to develop crystals between 100 m and 50 m, grows directly on the vesicle walls or sometimes preceded by the smectite phase. In many instances, it forms a continues isotropic rim enclosing palagonite clasts and preceding the crystallization of phillipsite. This was previously interpreted by Dwairi (1987) as an amorphous aluminosilicate gel. Scanning electron microscopy shows that the mineral occurs in the form of octahedral crystals.

5. Phillipsite

Phillipsite occurs mainly as colorless, radiating crystal aggregates forming a thin rim on pyroclasts. It is also present as isolated euhedral stout prisms. Rosettes of radiating and spherulitic crystal form are typical. The pseudorthorhombic symmetry is evident from the two-sided dome terminating crystals (Mumpton and Ormsby, 1976). Crystals are commonly less than 50 m long and rarely as long as 300 μm.

6. Chabazite

Chabazite occurs in transparent, isolated or clustered, equant, rhombic, crystals with a rhombohedral cleavage, simple penetration twining and zoning. Crystals vary in grain size from several microns up to 200 μm.

7. Calcite

Calcite which represents the latest phase of authigenic minerals, occurs in the form of rim and blocky cement, filling central parts of vesicles and the intergranular space.

Paragenesis of Authigenic Minerals

The order of paragenesis of the principal authigenic minerals in the Aritayn Volcaniclastic Formation, determined based on petrographic and scanning electron microscopy aided with electron microprobe analysis and microchemical mapping by Ibrahim and Hall (1996) is as follows:-

Fresh sideromelane ⇒ palagonite ⇒ Mg-clay ⇒ faujasite ⇒ phillipsite ⇒ chabazite ⇒ calcite.

Ibrahim and Hall (1995) indicated that authigenic minerals were deposited in the same sequence. Where one or more of the minerals is absent, the remaining minerals retain the same sequence.

Quantification of Zeolite and calcite

Using the sizing and specific gravity methods of De Gennaro and franko (1979) and Mondale et al. (1988) pure phillipsite, faujasite and chabazite were separated from samples and used as XRD standard. The XRD indicate that the zeolite minerals are phillipsite, faujasite and chabasite (Table 2 and 3). Chemical analyses of some selected sample from zeolitic tuff are shown in Table 4.

Table 2.
X-Ray Diffraction Analysis

Sample No.	Ph	He	Cc	Au	F	Fa	Ch	Sm	G
TZ /001/TS	***	*	*	**	***	--**	--**	--*	--
TZ002/TS	**	*	*	**	***	*	--**	--*	--*
TZ/ 003/TS	***	*	*	**	***	--*	--***	-*-	--
TZ/ 004/TS	***	*	*	**	***	--*	--***	-*-	--
TZ/ 005/TS	***	*	*	***	**	*	***	*--	--
TZ/ 006/TS	***	*	*	**	***	--*	-**-	*	--
TZ/ 007/TS	***	*	**	**	***	--*	--***	*	--
TZ /008/TS	*	*	**	***	**	*	***	--*	*

Note:Key: Based on Relative (X.R.D) High Peak Data Major: *** Minor: ** Trace: *
Ph=Phillipsite Fa=Faujasite Ch=Chabazite Au=Augite Cc=Calcite
F=Feldspar G=Gypsum He=Hematite Sm=Smectite

The results of the quantified zeolites and calcite are shown in Table 3. The percent of phillipsite varies from 18.44 to 44.10%, chabasite from 23.75 to 27.72%, faujasite from 0 to 6.32%, calcite from 5.24 to 22.91% and the pyroclasts from 20.72 to 47.63%. The total percentage of the zeolite minerals in the study area is between 42.19 and 70.19%.

Summary and Conclusions

A detailed petrographic, mineralogical and geochemical investigations including XRD, XRF, optical, electron microscopy, binocular microscope, polarizing microscope and SEM were carried out on the samples of new localities in northeast Jordan to understand the nature of the zeolite minerals of these deposits. The new zeolitic tuff deposits are of commercial value due to the high content of the zeolite minerals, contain large grain size zeolite minerals, relatively poorly lithified and porous. These properties are all favourable for successful beneficiation. Experimental investigations on the zeolitic tuff emphasized the importance of the Jordanian zeolites for use in wastewater treatment plants and as a soil conditioner and as slow-release fertilizer.

Table 3.
The zeolite, calcite and pyroclastic percentage in the study area using calibration curve

Sample No.	Phillipsite %	Chabasite %	Faujasite %	Calcite %	Total % of Zeolite	Pyroclasts
BH1/1	23.57	24.42	0.00	5.93	47.99	46.08
BH2/1	23.57	26.44	0.00	15.65	50.01	34.34
BH2/2	23.23	24.35	5.58	7.07	53.15	39.78
BH3/1	31.78	26.67	0.00	8.01	58.45	33.54
BH3/2	24.25	25.62	0.00	5.24	49.87	44.89
BH4/1	24.25	25.92	6.32	7.07	56.49	36.44
BH4/2	18.44	23.75	0.00	22.91	42.19	34.91
BH6/1	24.94	26.74	0.00	10.41	51.68	37.91
BH6/2	43.07	27.12	0.00	9.09	70.19	20.72
BH6/3	40.34	27.72	0.00	9.09	68.05	22.86
BH6/4	44.10	25.55	0.00	3.72	69.65	26.63
BH6/5	28.36	26.44	0.00	6.63	54.80	38.57
BH6/6	20.49	25.70	0.00	6.18	46.19	47.63
BH7/1	25.96	27.49	0.00	5.05	53.46	41.50
BH7/2	26.99	25.17	0.00	5.43	52.16	42.41
TZ/BH6	27.68	26.29	0.00	6.56	53.97	39.47
BH10/1	31.10	25.40	0.00	7.76	56.49	35.74
BH10/2	28.02	25.17	0.00	7.45	53.19	39.36

Table 4.
Complete Chemical Analysis from the boreholes

Sample No.	L.O.I%	Fe_2O_3%	CaO%	K_2O%	Na_2O%	SiO_2%	Al_2O_3%	MgO%
TZ/BH1/001/TS	15.79	12.15	5.75	2.21	1.33	42.68	13.71	5.57
TZ/BH2/001/TS	12.63	13.89	8.59	1.78	1.49	42.45	11.88	6.11
TZ/BH2/002/TS	15.03	12.06	5.13	2.14	1.44	42.94	13.23	6.38
TZ/BH3/001/TS	8.97	15.06	5.16	2.04	1.95	47.63	12.03	6.16
TZ/BH3/002/TS	12.49	13.56	4.50	2.24	1.84	43.69	12.87	6.81
TZ/BH4/001/TS	15.07	10.86	7.48	1.78	2.18	42.42	12.88	5.52
TZ/BH4/002/TS	14.36	10.43	14.79	0.45	1.02	40.77	12.15	4.24
TZ/BH6/001/TS	9.15	13.23	4.13	1.37	2.54	47.90	12.05	7.75
TZ/BH6/002/TS	9.44	12.98	6.28	2.12	2.02	43.72	13.9	7.94
TZ/BH6/003/TS	10.90	13.13	7.50	2.03	1.94	42.32	12.66	8.58
TZ/BH6/004/TS	10.96	13.16	6.11	1.60	1.75	43.55	12.54	8.57
TZ/BH6/005/TS	11.53	14.74	2.9	1.43	1.29	45.89	10.35	8.62
TZ/BH6/006/TS	11.93	14.73	3.90	1.81	1.24	43.66	12.45	8.40
TZ/BH7/001/TS	12.46	12.59	4.21	2.21	2.29	47.52	12.10	6.51
TZ/BH7/002/TS	12.23	12.60	4.62	2.44	2.13	48.21	12.11	5.35

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