

## THE MINERALOGIC, PETROGRAPHIC AND ION EXCHANGE CAPACITY FEATURES OF TUFFS CONTAINING CHABAZITE AND PHILLIPSITE MINERALS IN SANDIKLI (AFYON) REGION AND THEIR USAGE IN AGRICULTURE (SOUTHWEST ANATOLIA, TURKEY)

Yahya ÖZPINAR\*

**ABSTRACT.-** The study area is located at southern part of Sandıklı town (Afyon-southwest Anatolia). The volcanics of Sandıklı region in the investigated area are represented by lavas and pyroclastic rocks of Middle-Late Miocene age. The Lavas occur as trachyandesitic, phonolitic tephritic, basaltic andesitic, basaltic trachy-nephelinitic, andesitic and dacitic in compositions. Pyroclastic rocks are composed of lapillistone, tuffaceous conglomerate, tuffaceous sandstone, tuffaceous siltstone and tuffaceous mudstone, and also have vitric and crystal vitric tuffs in trachyandesitic, phonolitic and tephritic compositions. In the tuffs located at the northern part of the investigated area the chabazite occurrences, and in the tuffs located at the southern part the phillipsite occurrences are found widespreadly. In phillipsitic tuffs, three-phillipsite forms were defined namely potassium-sodium-aluminum-silicate hydrate, sodium-aluminum-silicate hydrate and potassium-calcium-aluminum-silicate hydrate forms. In tuff samples purified with tetrabrom ethane the zeolite contents by weight mostly between 29.00 wt.% and 63.00 wt.%. After the activation of the tuff samples with 0.1N HCl and 0.1N H<sub>2</sub>SO<sub>4</sub>, their cation exchange features were investigated. In the tuffs activated with both acids, Ca<sup>+2</sup> content with respect to other cation contents has been passed too much to the solutions depending on time. But those activated with 0.1N HCl, as depending on time, Ca<sup>+2</sup> content has been passed as more linear to the solutions. When we consider of ion exchange capacity and selection of the radioactive cations such as <sup>137</sup>Cs and <sup>90</sup>Sr and <sup>40</sup>K of chabazite and phillipsite, zeolitic tuffs may be used for improvement of soil, stabilization of pH of acidic soils and to prevent to passing of the radioactive elements from nature to the environment and biological systems. Because of activated natural zeolites tend to the increasing of the resorption and adsorption of moisture which contributes to the plant development, activated natural zeolitic tuffs may be used as desiccants. For the adsorption of the ammonium smells arised from urine and fecal matter, it is thought that zeolitic tuffs may be used to separate methane from other gasses. Besides, it is believed that it is possible to use them as building stone for heating and air conditioner for small houses and animal shelters.

**Keywords:** Chabazitic and phillipsitic tuffs, Sandıklı, Southwest Anatolia.

### INTRODUCTION

The investigated area is located at southern part of Sandıklı town. The Sandıklı is the town of Afyon city and situated at the western part of Central Anatolia in Turkey (Figure 1). This study comprises part of investigations supported by TUBITAK "YDABÇAĞ-198Y102". In this project, geological, petrographical and mineralogical features of Sandıklı volcanics were investigated and experiments were made to determine technological usage of tuff and tuffites. However the purpose of this paper is to report the results of detailed

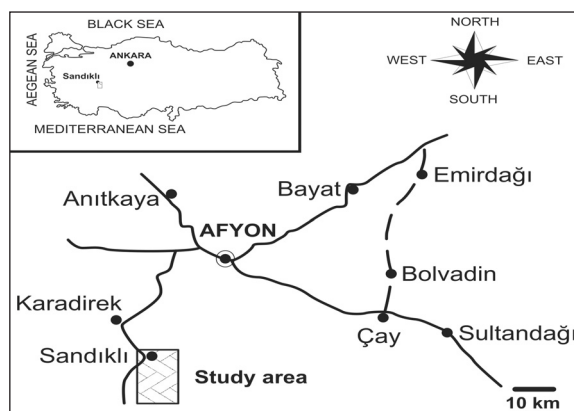


Figure 1- Location map of the study area.

\*Pamukkale Üniversitesi, Mühendislik Fakültesi, Jeoloji Müh. Bölümü, Kınıklı Kampüsü, 20017, Denizli.

study of mineralogic, petrographic and ion exchange capacity features of tuffs containing of chabazite and phillipsite minerals at southern part of Sandıklı town and their evaluation for healthing.

The investigated area and its surrounding districts have been studied by many investigators based on investigation topics. Some of these studies can be grouped as following. The Afyon and Sandıklı Neogene basins and hydrogeological feature of Hüdai geothermal area in Sandıklı region have been studied by Ronner (1962), Bulutcu (1975) and Afşin (1991) and they pointed out that the Hüdai geothermal water have high radioactive features. The geological and petrological features of Afyon and Sandıklı volcanics of Middle and Late Miocene age, namely trachyte, thrachyandesite, rhyolite, latite and basalt having alkaline and calk-alkaline character have been studied by Villari and Keller (1972), Keller (1983), Öngür (1973), Başarır and Kun (1982) and Ercan (1986). Using the K-Ar age method, of the Sandıklı volcanics have been dated by Besang et al. (1977) and obtained the ages  $14\pm 0.3$ - to  $8.0\pm 0.6$  Ma. Çoban and Flower (2007) asserted that the magmatism in the Kirka-Afyon-Isparta region shows a temporal progression from calk-alkaline to ultrapotassic affinity which is associated with the geodynamic evolution of the "Isparta Angle". The petrological evolution and lamprophyres of Afyon stratovolcano have been investigated by Aydar et al. (1996, 2003). Tectonic and metamorphic evolutions of Sandıklı-Afyon region have been studied by Öngür (1973) and Tolluoğlu et al. (1997). Zeolitization in Sandıklı tuffs, firstly has been discovered by author (Özpinar, 1998; Özpinar et al. 1998). In addition, Özpinar et al. (2002) studied petrographic and petrochemical features of zeolitic tuffs at southern part of Sandıklı region.

## METHOD OF STUDY

In this study, for determining the distribution of Sandıklı volcanics, detailed mapping of an area

about 180 km<sup>2</sup> was firstly done at 1/25 000 scale and microscopic studies of 98 samples were carried out. Later, for all study 101 samples of lavas, tuffs and tuffites were qualitatively determined by XRD and zeolites specimens purified with heavy liquid (tetrabrom ethane) qualitatively determined by DTA (10 sample) and electron microscope (8 sample) and chemical analyses of the altered lavas, tuffs and tuffites (58 sample) were carried out by XRF in R&D laboratories of Turkish Cement Manufacturer's Association. In addition the chemical analyses of the lavas (8 sample) and tuffs (2 samples) were carried out by ICP-MS in Acme Analytical Laboratories Ltd., Canada. Beside, cation exchange capacity tests were carried out by flame photometry (JENWAY mark) apparatus in laboratory geological engineering department of Pamukkale University.

## STRATIGRAPHY AND PETROGRAPHY

In the study area the Karatepe formation represented by violet colored conglomerate and siltstone of Late Triassic-Early Jurassic age is exposed at the bottom of the sequence and well observed southwest of Yeniçay located at the western part of the area (Figure 2). The Karatepe formation is transitionally overlain by Derealanı formation of Jurassic age which is also transitionally overlain by Akdağ formation of Late Jurassic- Early Cretaceous age exposed at the mountainous areas of the southern and southeastern part of Sandıklı region. From lower to upper parts, the Akdağ formation is represented by gray and dark gray colored micritic and cherty limestones, respectively.

The Akdağ Formation is unconformably overlain by Neogene age units. Lacustrine detritic rocks of Middle(?) - Late Miocene age is located at the lower part of lithologic units and composed of conglomerate, sandstone, marl and limestone. This unite is unconformably overlain by the detritic rocks of Quaternary represented by gravel, sand and clay (Figure 2 and 3).

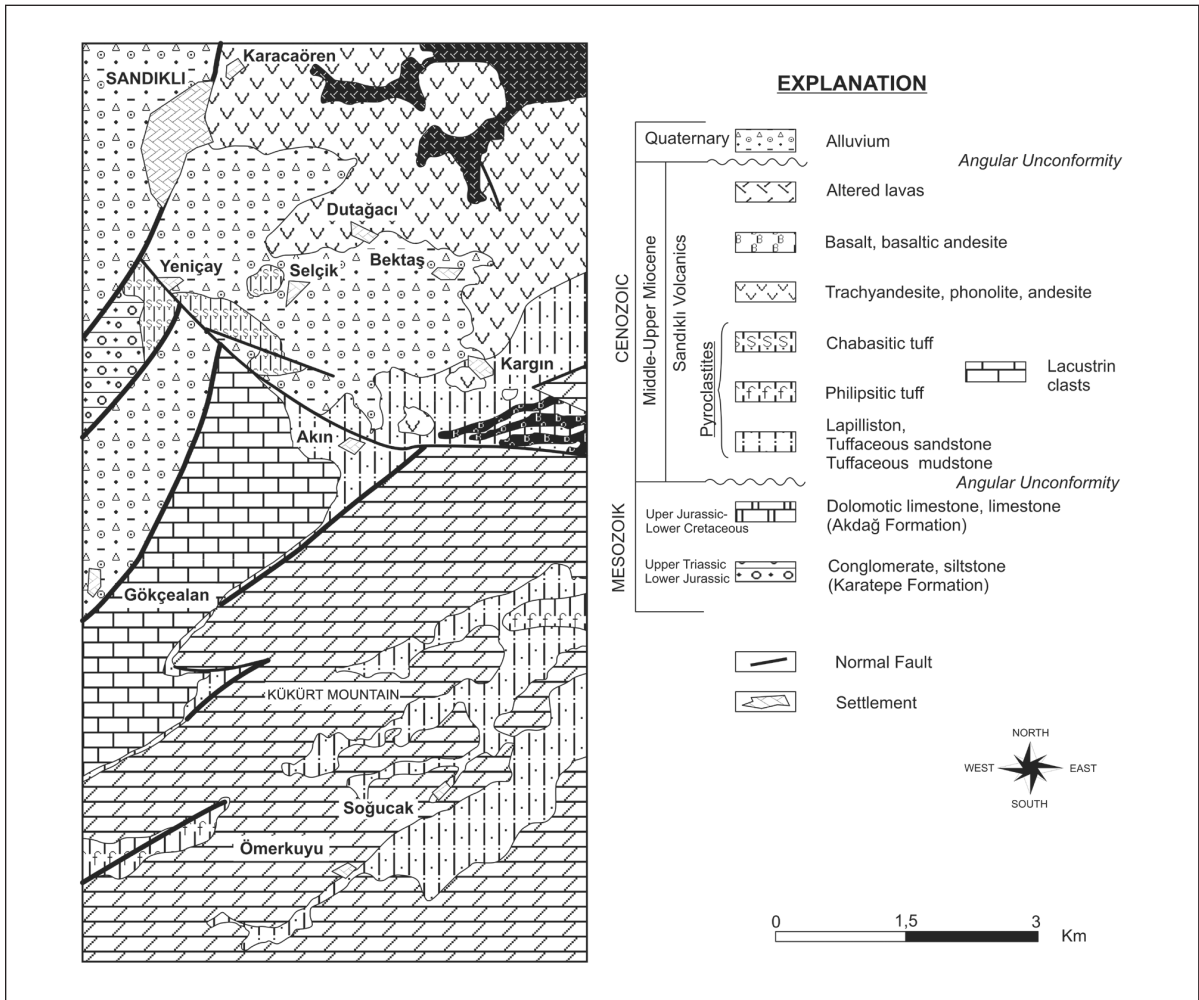


Figure 2- Geological map of the study area.

In the study area, the Middle-Late Miocene volcanics and volcano-sedimentary units have been named as Sandıklı volcanics. By using the radiometric age method, the age of Sandıklı Lavas have been dated by Besang et al. (1977) and the ages obtained range between  $14 \pm 0.3$  -  $8.0 \pm 0.6$  Ma (Ercan, 1986). The Sandıklı volcanics are mainly composed of red, gray and light brown colored lavas and pyroclastic rocks ( Figure 2 and 3).

The pyroclastic rocks have various ratio of pyroclastites, epiclastites (Schmidt, 1981), pyrogenetic and secondary minerals. The pyroclastic

rocks are named as lapillistone, tuffaceous conglomerate, tuffaceous sandstone, tuffaceous siltstone and tuffaceous mudstone. The coarse grained pyroclastic rocks are found at lower part of the sequence. At bottom, lapilli could become thrachyandesitic rock pieces and also could become white and gray colored pumice pieces (Figure 4). The matrix generally comprises fine and coarse grained volcanic ash. Above these rocks the tuffaceous sandstone overlies which contains few sand sized epiclasts and at the upper levels of sequence the tuffaceous mudstone is present (Schmidt, 1981; Fisher and Schmincke, 1984).

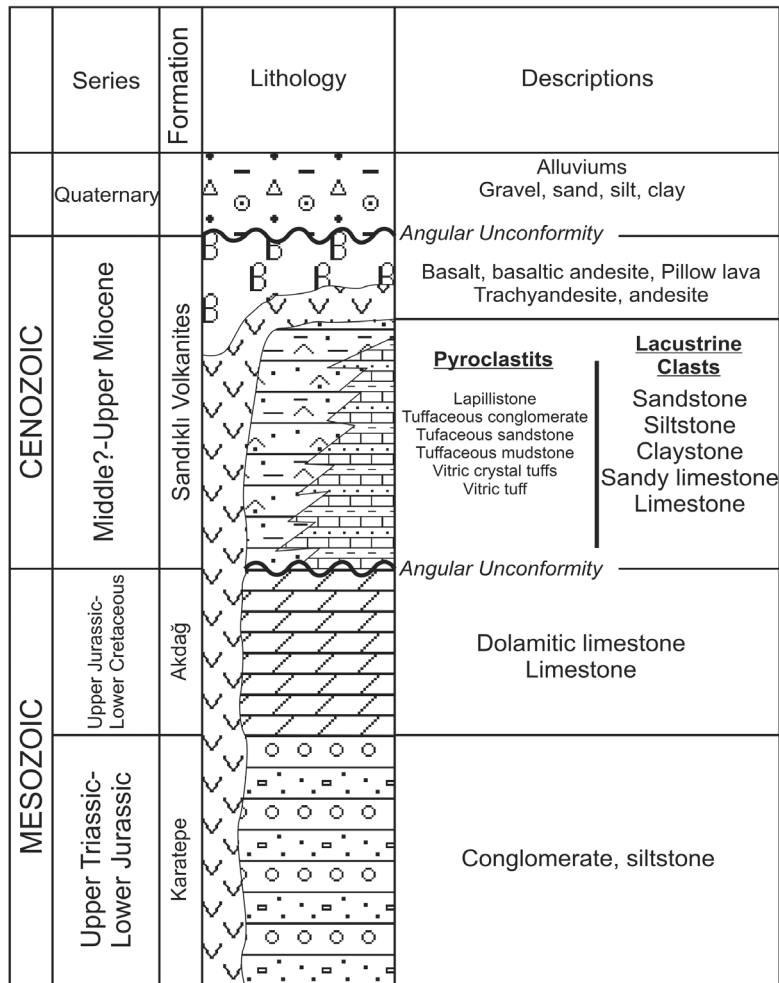


Figure 3- The simplified schematic columnar section of the study area, (not to scale).

Tuffs are exposed at southern and northern parts of investigated area. They have trachyandesitic, phonolitic and tephritic compositions (Özpinar, 2001; Özpinar et al., 2002) named as vitric tuff and crystal vitric tuff. As depending on zeolite type (chabazite and phillipsite), zeolitic tuffs indicate different textural and structural features.

Chabazitic tuffs have cream colored, consolidated components and contain high porosity which are exposed at northern part of investigated area (south and west of Selçik village). According to identification by optical microscope, they

have pyroclasts and epiclast in various ratio and sizes. In the tuffs, pyroclasts have microlitic and micro-porphyric texture. In the pyroclasts, plagioclase and augite are found as microlite and phenocrystals. As a result, cream colored tuffs contain sanidine, albite, augite, biotite, clay minerals (illite), zeolite (chabazite) chlorite, opaque minerals and iron oxide. These minerals have also been determined by X-ray diffractometer.

Phillipsitic tuffs are gray, dark gray and brownish in color and have extremely consolidated components and high specific density than cha-



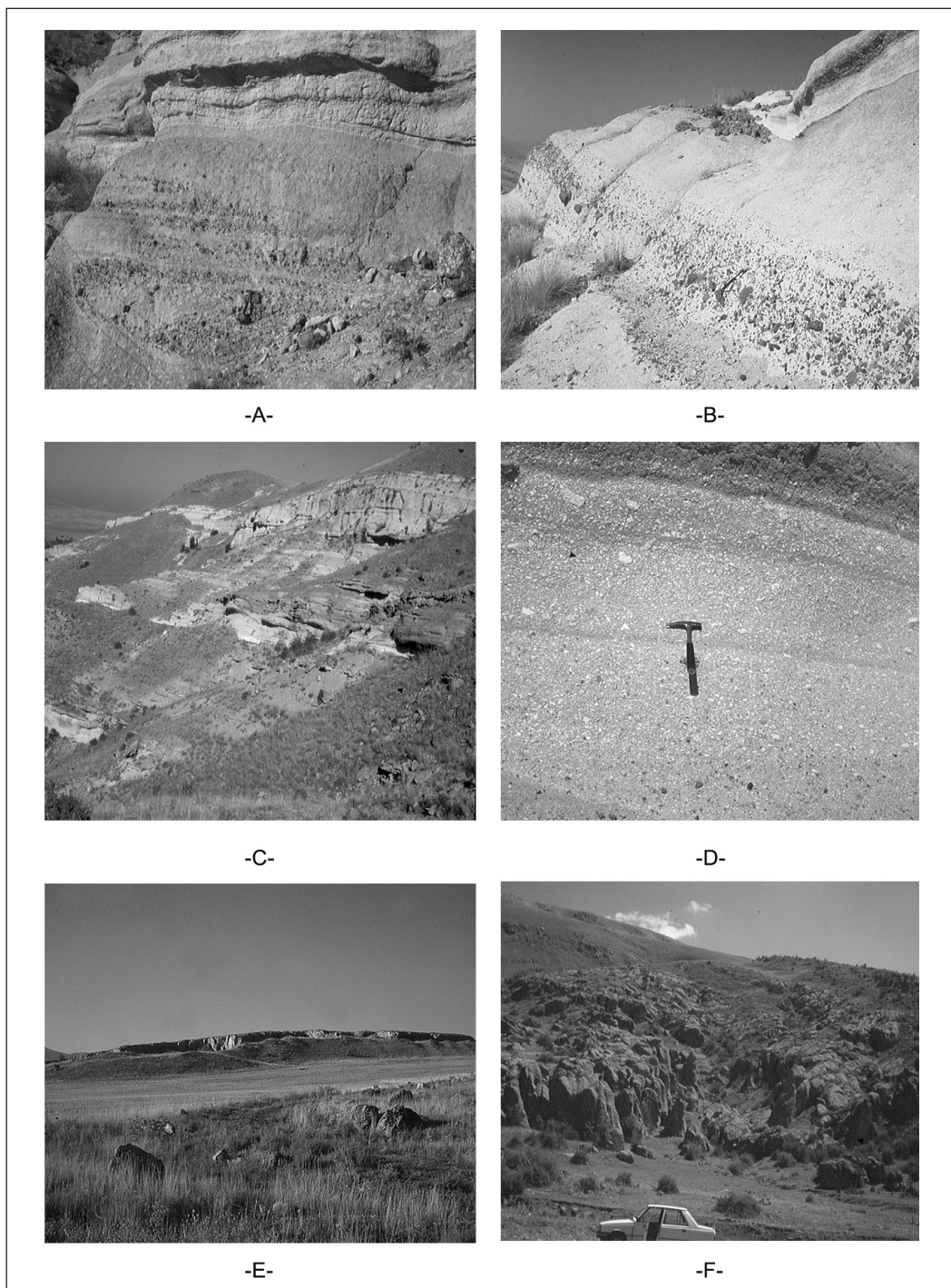


Figure 4- Field views from pyroclastic rocks. A, B and C) Tuffaceous conglomerate, tuffaceous sandstone, tuffaceous siltstone and tuffaceous mudstone. D) Tuffaceous lapillistone with rhyodacitic pumice E) Cream colored tuffs located at northern part of study area and F) Dark gray and brownish colored tuffs located at southern part of study area.

bazitic tuffs. These are exposed at southern part of study area and located at Ballık, Ömerkuyu and Soğucak village, Sütlüce Küfeke tepe and its surrounding area. In the gray, dark gray and brownish tuffs, pyroclasts have microlitic and porphyritic texture. In addition, they have fine gravel and coarse sand sized and reworked and partly rounded. Beside, the tuffs contain a few radiolarite fragments which are partly rounded. The Soğucak tuffs have fine gravel and coarse sand sized particles of basaltic and trachy-basaltic compositions and Fe-oxide alteration is commonly seen. In Sütlüce Kufeke hill area, tuffs present columnar structure and they have lesser

pyrogenic minerals and contain partly microcrystalline limestone "micrite" (Folk, 1962). The pumice contents are too much. According to the identification by optical microscope, the phillipsitic tuffs contain plagioclase (albite), augite, zeolite (phillipsite), biotite, clorite, calcite and iron oxide (Figure 5 and 6). These minerals have also been determined by X-ray diffractograms. In gray, dark gray and brownish tuffs, three phillipsite form were determined. These are potassium-sodium-aluminum-silicate hydrate, potasium-aluminum-silicate hydrate and potassium-calcium-aluminum-silicate hydrate.

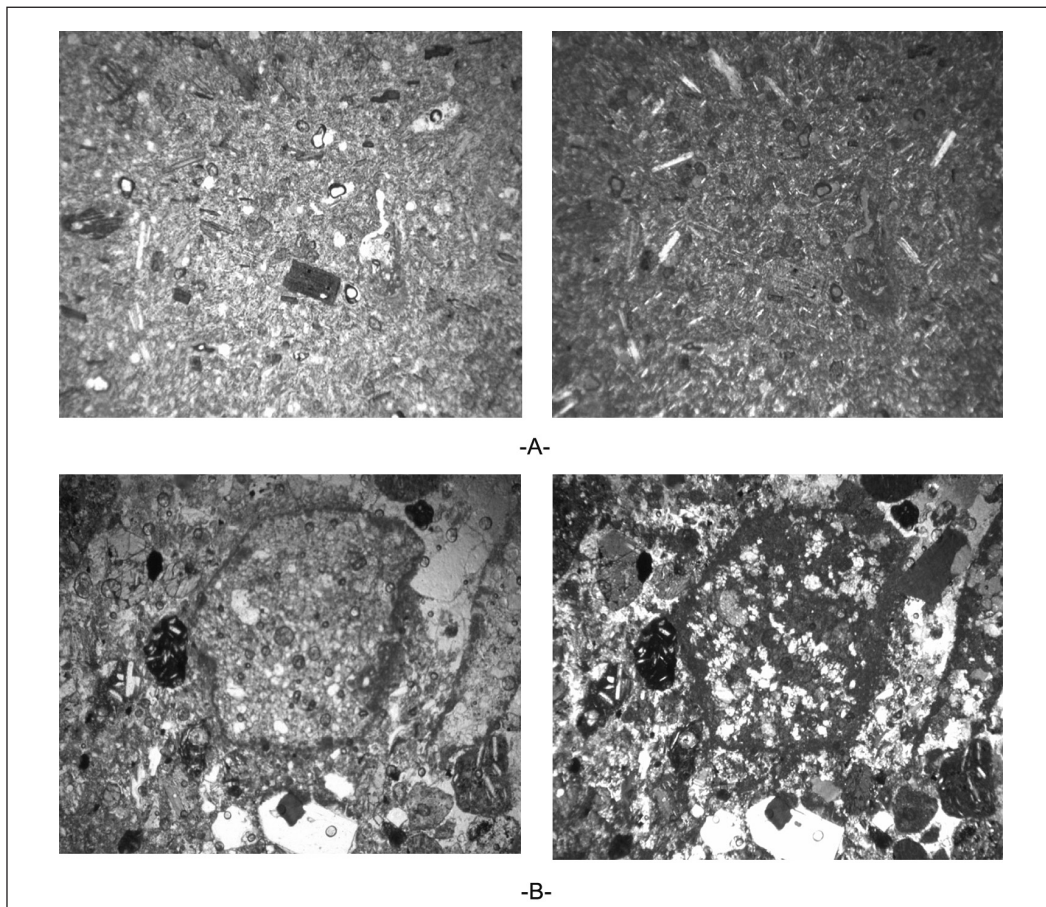


Figure 5- Microscopic views of vitric and crystal tuff (A), zeolitization of in pyroclasts and glassy matrix (B). Microscopic views at single (on the left) and double nicol (on the right) prism (A: 40X. B: 100X)



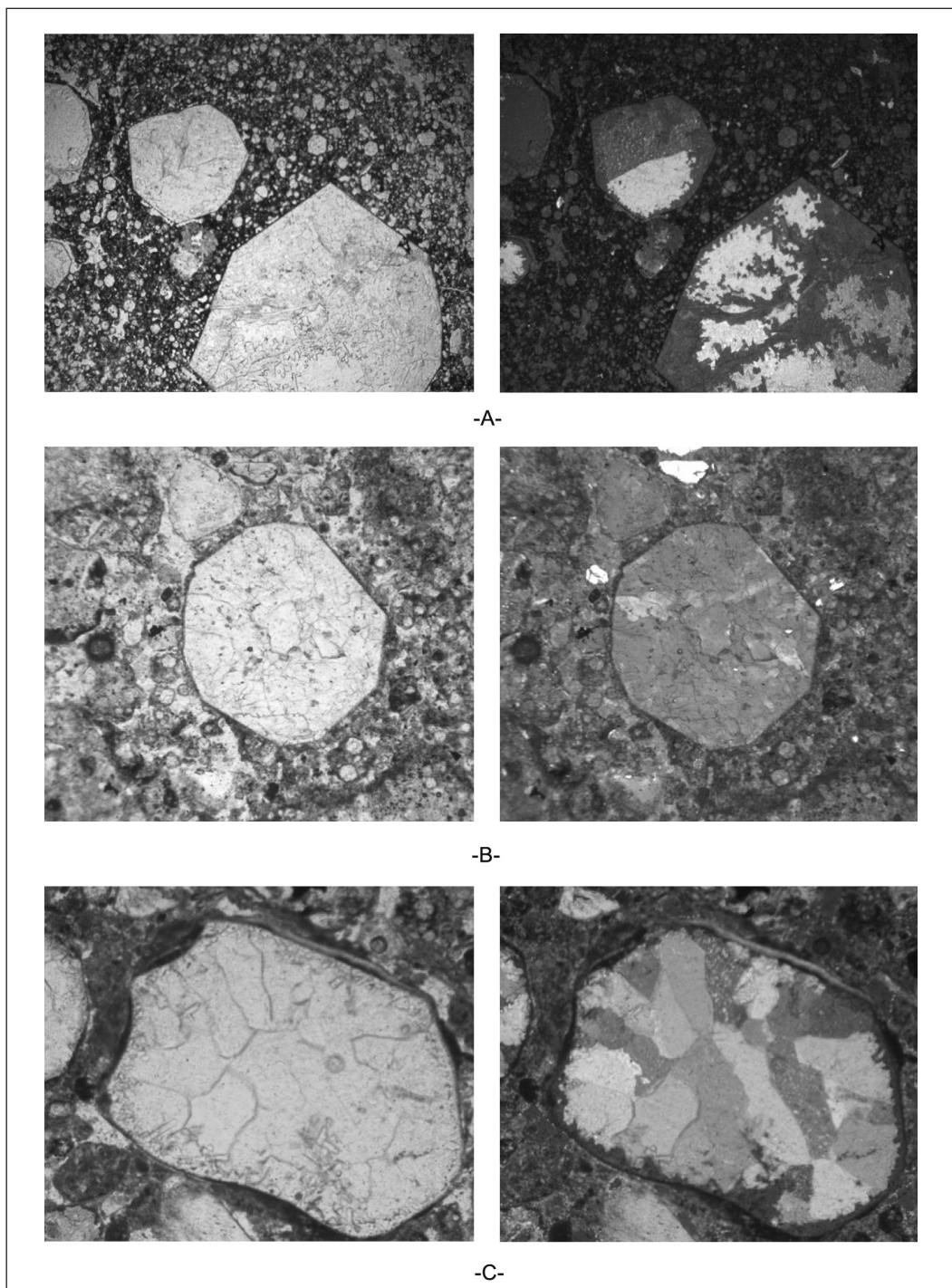


Figure 6- Thin section views of zeolitic tuffs. Zeolites have been seen with pseudo-hexagonal and isometric dodecahedron forms, under the microscope (A and B), large grain zeolite minerals (C) microscopic views from single (on the left) and double nicol (on the right) prism (100X)

In these area, phillipsites genarally have K, Na- form and K-form and besides K, Ca-form is lesser than the other form. In these tuffs, zeolitization of Soğucak location is too much and at some locations, ratio of zeolitization approach to 80% and 85%.

Sandıklı lavas have trachyandesitic, phonolitic tephritic, basaltic andesitic, basaltic trachynephelinitic, andesitic and dacitic compositions (Özpinar , 2001., Özpinar et al., 2002), mineralogic composition and textural features of andesite and trachyandesite specimens is essentially pilotaxitic, hyalopilitic, hyalo-porphyritic and micro-porphyritic. Groundmass essentially consists of fine and medium sized plagioclase microclites in a glassy matrix. Sanidine, plagioclase (oligoclase), biotite, basaltic hornblende occur as phenocrysts. The sanidine phenocrysts determined in the samples have very large sizes (from 3 to 5 cm). Apatite, sphene and zircon can be observed as accessory minerals. The chlorite and calcites have been found as secondary minerals. The results of microscopic and X-ray diffractograms are similar. Quartz, albite, sanidine, orthoclase, augite, biotite and illite from the mineralogic composition of the samples in general.

In some locations located at the northern part of the investigated area, the lavas of andesitic and trachyandesitic compositions have been extensively altered by hydrothermal solutions (Figure 7) and changed to the clay (illite) and zeolite (chabazite) minerals. The zeolite formation of altered lavas is small in amount. In lavas where alteration is less, the zeolite mineral is not found. In altered lavas, the following minerals were identified by optical microscope and X-ray diffractograms; sanidine, plagioclase (albite), basaltic hornblende, biotite, chlorite, illite, montmorillonite (in some specimens), zeolite (chabazite), calcite, opaque minerals and iron oxide.

#### SEPERATION OF ZEOLITE MINERALS FROM TUFFS BY USING HEAVY LIQUID

Firstly, mineralogic composition and textural features of the zeolitic tuff specimens were defined under the polarized microscope. Later the specimens were investigated by X-ray diffraction method. Secondly, by using heavy liquid (tetrabrom ethane), the zeolite minerals were purified from zeolitic tuffs (Minato, 1992). The separation process used by heavy liquid is as following; sample is crushed to fine powder in agate mortar. The fine powder (clay minerals) is dispersed in a

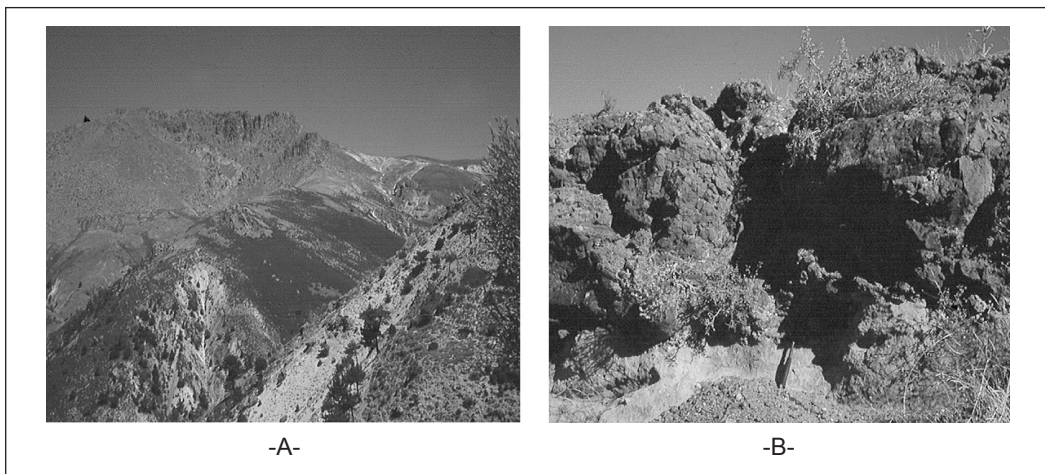


Figure 7- A) Field views of trachyandesitic and altered trachyandesitic lavas (A) and basalts (B).



distilled water by ultrasonic vibrator in beaker and are filtered by filter paper and dry up at about 60°C. Heavy liquid separation processes are carried out by using tetrabrom ethane. Purified zeolite grains are filtered by filter paper and washed by acetone and dried up. The purified zeolite grains are analyzed by X-ray diffraction method. At this method, if zeolite minerals have large grains, it can be obtained higher rate of success. According to the results which have been arranged, the amount of chabazite as weight % are 55.86 %, 29.00 %, 58.93 % and 42.4 % (Sample numbers: Z-2, Z-3, Z-6, Z-8) respectively. The amount of phillipsite as weight % are 62.40 %, 63.0 %, 51.53 % and 61.86 % (sample numbers: Z-1, Z-4, Z-5, Z-7) respectively.

### Investigation of Zeolite Minerals by Electron Microscope and X-Ray Diffraction Method

The purified zeolite specimens were tested by means of X-ray diffraction method. According to X-ray diffractograms, determined minerals are given at table 1, figure 9 and 10. As mentioned above, while the tuffs located at Selçik village and its surrounding area contain only chabazite, the tuffs located at Ballık village (Table 1) and its surrounding area contain chabazite and phillipsite, and tuffs located at Alılı, Soğucak, Ömerkuyu and Sütlüce Küfeke and their surrounding area contain only phillipsite. In addition, three-phillipsite forms were determined. These are potassium-sodium-aluminum-silicate hydrate, pota-

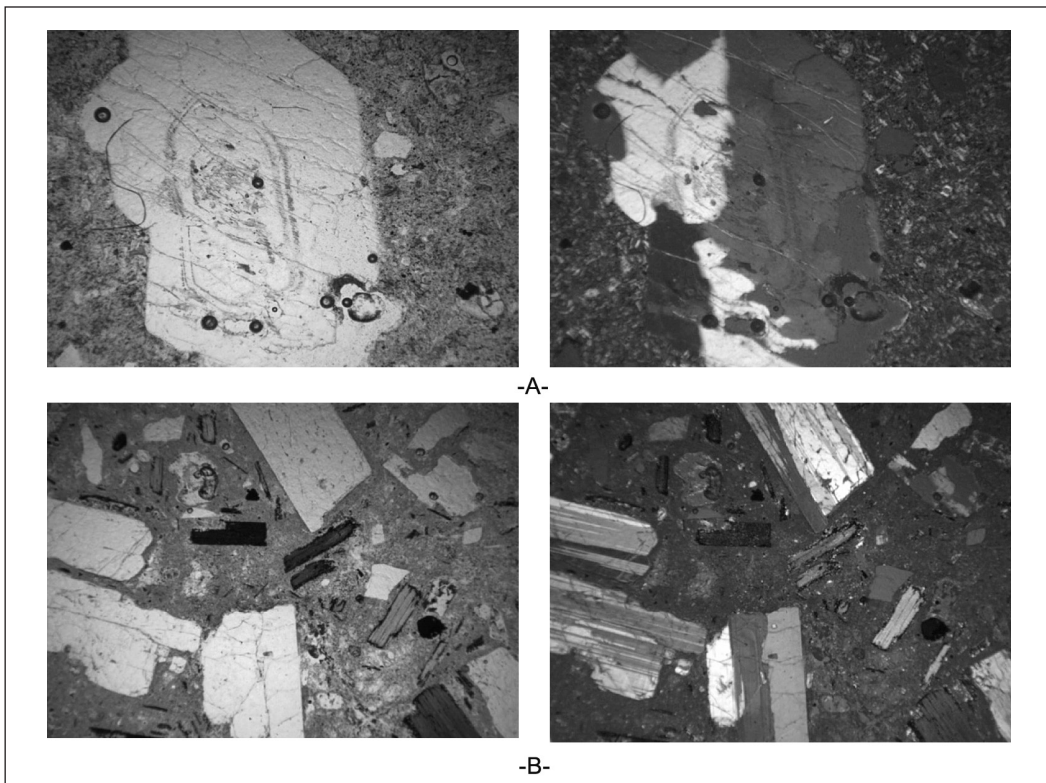


Figure 8- Microscopic views from trachyandesitic (A) and andesite (B) Large sanidine crystal from trachyandesite specimen (A) and biotite and plagioclase crystals from andesite specimens (B). Microscopic views from single (on the left) and double nicol (on the right) prism, 40 X.

sium-aluminum-silicate hydrate and potassium-calcium-aluminum-silicate hydrate. While in tuffs of southern part of investigated area three form of phillipsite have been determined, in tuffs of Sütlüce Küfeke tepe and its surrounding area two phillipsite form have been observed. These are potassium-sodium-aluminum-silicate hydrate and potassium-calcium-aluminum-silicate hydrate.

As mentioned above, if zeolite minerals have large grains, it can be obtained higher rate of success. In southern part of study area tuffs, zeolite minerals are large grains than zeolite minerals of northern part of study area. Because of

this, at purified processes of phillipsitic tuffs became with a few errors, these results can be seen in table 1. Appearances under the electron microscope (SEM) and their EDS spectrums of phillipsite (Z-1) and chabazite (Z-8) are given in figure 10.

### Thermal Features of the Zeolite Minerals

The different data were obtained from thermograms of zeolite minerals purified by heavy liquid (Figure 11), In thermograms of chabazite specimens, the first endothermic peaks at temperature of 178 °C, 186 °C and 234 °C show maximum water loss. Second endothermic

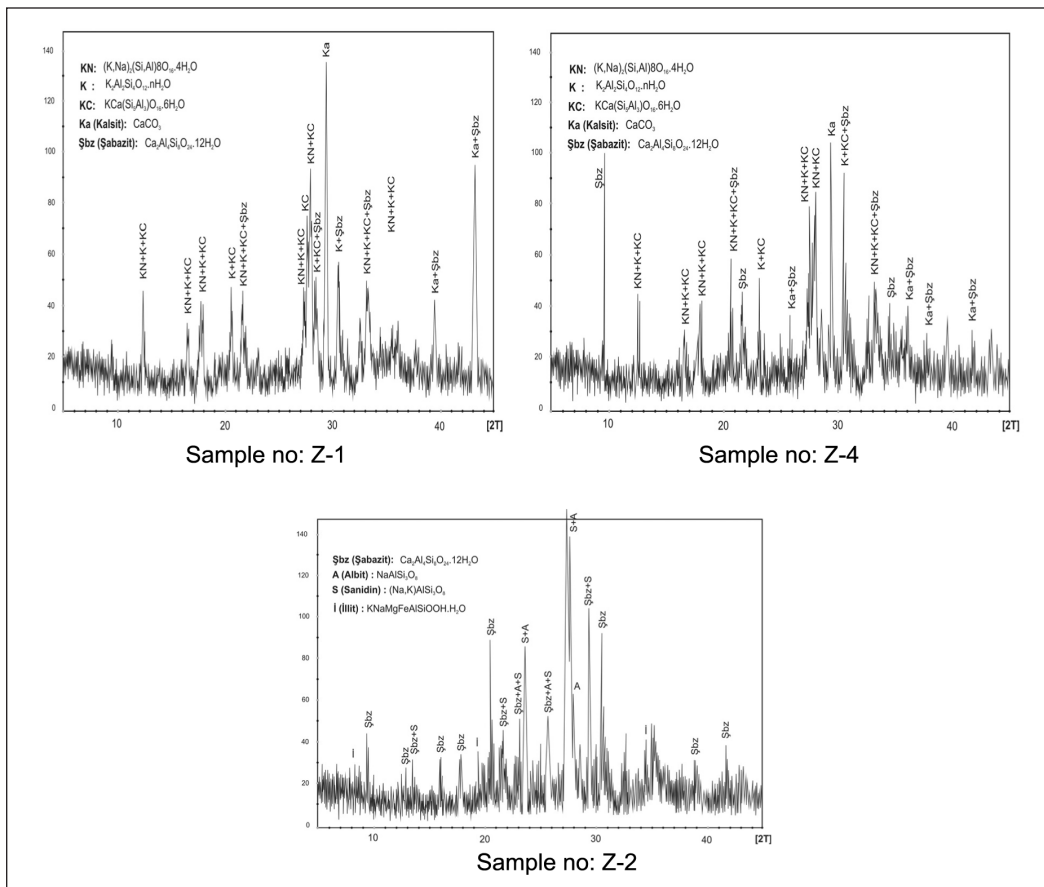


Figure 9- After separation processes with heavy liquite, mineralogic composition of determined by means X-ray diffractogram (A: albite; S: sanidine, Ca: calcite, Ch: chabazite, phillipsite (KN: K, Na form, K: K form, KC: K, Ca form)).

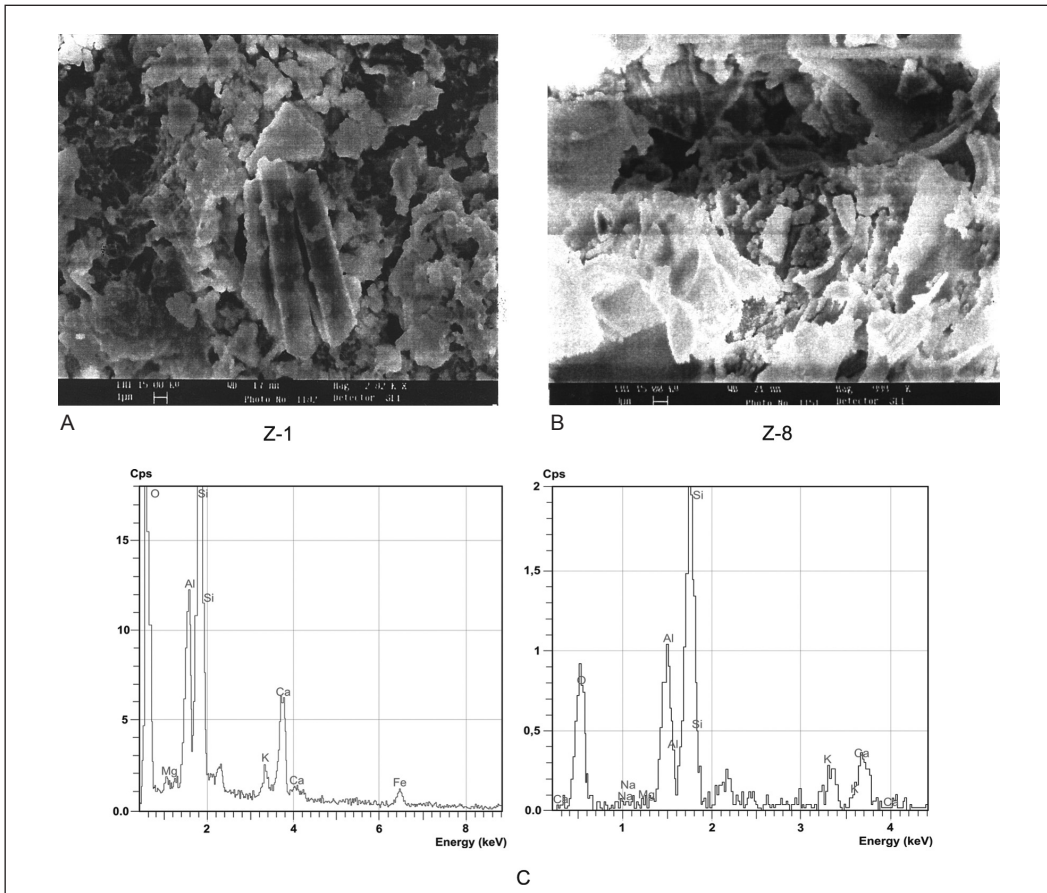


Figure 10- A: Phillipsite (Z-1) B: chabazite (Z-8) SEM and C: Their EDS spectrums.

peaks show that the dehydration ends at temperature of 446 °C and 552 °C. Third endothermic peaks occurred at temperatures of 717 °C and 742 °C. These peaks indicate that due to narrowing of channels and breakdown of connected with the loss of huge free surface of dehydrated channels. Exothermic peaks at temperature of 846 °C ile 879 °C are associated with breakdown of sample mass change considerably. In all chabazite samples approximately at 1000 °C mass loss by weight occurred 12.5 % (Figure 11).

According to phillipsite forms, loss of water in phillipsite samples occurs at 70 °C, 120 °C, 140°C, 180 °C and 320 °C. In addition, It is con-

cluded that endothermic peaks at 205 °C and 280 °C are not sharper peaks. The endothermic peaks due to loss of water in philipsite samples of study area occurred at temperature of 155 °C and 272 °C. According to chemical forms of phillipsites, endothermic peaks make clear that dehydration ends in intervals of temperature at 415 °C and 536 °C. After these temperatures having been determined, metaphillipsite forms are protected and also exothermic peaks in intervals of temperature at 839 °C ve 879 °C and in all phillipsite samples mass loss of 12.7 % by weight were become approximately at 1000 °C (Figure 11).

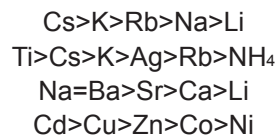


**Table 1- After separation processes with heavy liquite, mineralogic composition determined by means of X-ray diffractogram (Alb: albite; San: sanidine, Ort: orthoclase, Q: quartz, Cal: calcite, il:illite, He. hematite, Cha: chabazite, Phillipsite (K, Na form, K form, K, Ca form)).**

Samp le. No	MINERALOGICAL COMPOSITION										Locations and Sample numbers	
	Feldspars			Q	Kal.	İl.	He.	ZeolitE Minerals.				
	Alb.	San	Ort.					Cha.	KN	K		KC
Z-1					+			+	+	+	+	Ballık tuffs, Sample Num:ST-11,12
Z-2	+	+		+	+			+				Selçik tuffs, sample num.: ST-25,26,27
Z-3	+	+		+				+				Selçik tuffs, Sample num.: :ST-1,2,3,4
Z-4					+			+	+	+	+	Ballık tuffs, Sample num.: : ST-13,14
Z-5			+						+	+	+	Soğucak tuffs, sample num.: ST- 16,17
Z-6	+	+		+	+			+				Southern part of Selçik , tuffs.Sample num.: : ST-24,25,26
Z-7					+		+		+		+	Sütlüce küfeki tepe tuffs . SAmple num.: ST:19,20
Z-8	+	+				+		+				Selcik tuffs Smples num.: S-109

## ION EXCHANGE FEATURES OF ZEOLITES

Depending on Si/Al ratios of chabazite structure, cations exchanged forms can be changed by temperatures and environmental conditions. According to Tsitsishvili et.al (1992), investigation of exchange reactions  $\text{Na} \leftrightarrow \text{K}$ ,  $\text{Na} \leftrightarrow \text{Cs}$  and  $\text{Cs} \leftrightarrow \text{K}$  at 250 °C showed that exchange for large cations causes the structure to become stable. Chabazite is known to be selective towards Cs (cesium). The stability of ion exchanged forms decreases in the series  $\text{Cs} > \text{K} > \text{Rb} > \text{Na}$ . Apart from Cs, other cations substitute up to 84% of Na ions in chabazite structure.  $\text{K}^{+1}$  ions are easily concentrated on chabazite from solutions containing high concentrations of  $\text{Na}^{+1}$  ions. The following selectivity series are known (Tsitsishvili et al. 1992).



In terms of ion exchange features, phillipsite behaves more selective towards  $\text{K}^{+1}$  and  $\text{Na}^{+1}$ . Na- form of phillipsite is selective for large cations. In addition, phillipsite is selective for  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$ . At high concentrations, the metals can be concentrated on  $\text{NH}_4$  phillipsite. The selections towards potassium ions in presence of  $\text{Na}^{+1}$ , and towards sodium ion in presence of  $\text{Ca}^{+2}$  are greater in lower temperatures. Phillipsite rich in silicon is more selective to cation  $\text{K}^{+1}$  in Na-K system and less so to in Na-Ca system. On different samples of phillipsite, in 0.1M solutions, selective series of  $\text{K}^{+1} > \text{N}^{+1} > \text{Ca}^{+2}$  are similar for all samples which do not depend on temperature (in range 35-70 °C), Tsitsishvili et al ( 1992). The following

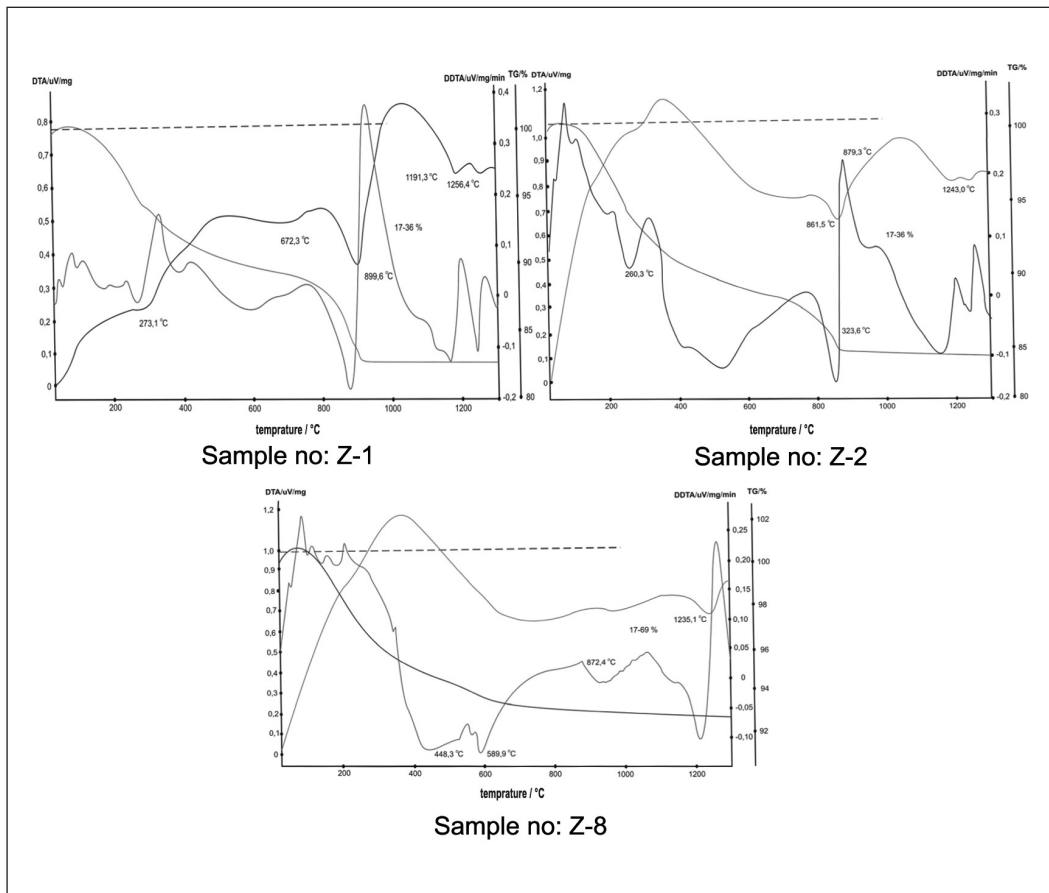
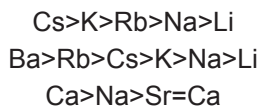


Figure 11- Thermograms of phillipsite chabazite (Sample num: Z-1) and chabazite (Sample num: Z-2, Z-8).

selectivity series are known (Tsitsishvili et al. 1992).



### INVESTIGATION OF CATION EXCHANGE FEATURES OF CHABAZITIC AND PHILLIPSITIC TUFFS IN THE STUDY AREA

The 0.1N HCl and 0.1N H<sub>2</sub>SO<sub>4</sub> solutions of 2.5 liters were prepared from each of the samples of cream coloured tuffs at Selçik and surrounding area and dark gray, brownish coloured tuffs at Balık-Soğucak-Ömerkuyu and Sütlüce Küfeke tepe. After this, 50 gram samples

were taken from both chabazitic and phillipsitic tuffs and settled in 0.1N HCl and 0.1N H<sub>2</sub>SO<sub>4</sub> solutions and shaken for two hours. After filtering the samples were washed by deionized water and dried up in an oven at 105 °C temperature.

For determining cation exchange capacity, 10 gr activated zeolitic tuff samples were taken and put in plastic bottles with NaCl, KCl, CaCl<sub>2</sub>, MgCl<sub>2</sub> and FeCl<sub>3</sub> solutions (500 ppm), and after this they were shaken 10 hours by hands. As using paper filter, solutions were filtered with interval two hours and analyses carried out by using flame photometry. From activated chabazitic tuffs with 0.1N H<sub>2</sub>SO<sub>4</sub>, depending on time, Ca<sup>+2</sup> content has been passed increasingly to the NaCl

and KCl solutions and decreasingly to the MgCl<sub>2</sub>, FeCl<sub>3</sub> solutions and also from activated chabazitic tuffs with 0.1N HCl, depending on time, Ca<sup>+2</sup> has been passed decreasingly to the KCl, NaCl, MgCl<sub>2</sub> and FeCl<sub>3</sub> solutions (Table 2 and Figure 12)

From phillipsitic tuffs activated (with 0.1N H<sub>2</sub>SO<sub>4</sub>, and 0.1N HCl) Ca<sup>+2</sup>, as depending on time Na<sup>+1</sup> ve K<sup>+1</sup> contents passing to the MgCl<sub>2</sub> and FeCl<sub>3</sub> solutions were obtained as quantitatively (mg/l), respectively. (Table 5 and Figure 13)

From phillipsitic tuffs activated with 0.1N H<sub>2</sub>SO<sub>4</sub> Ca<sup>+2</sup>, K<sup>+1</sup>, as depending on time, Ca<sup>+2</sup>, K<sup>+1</sup> content passing to the 500 ppm FeCl<sub>3</sub> solution have become too much than passing in 500 ppm MgCl<sub>2</sub> solution. In spite of this, Na<sup>+1</sup> content passing to the MgCl<sub>2</sub> solution have become too much than passing to the FeCl<sub>3</sub> solution (Table 4 and Figure 13).

On the other hand, Ca<sup>+2</sup>, K<sup>+1</sup> and Na<sup>+</sup> cations, from activated phillipsitic tuffs with 0.1N HCl, Ca<sup>+2</sup>, K<sup>+1</sup> and Na<sup>+1</sup> contents passing to the MgCl<sub>2</sub> solutions have become a decrease as depending

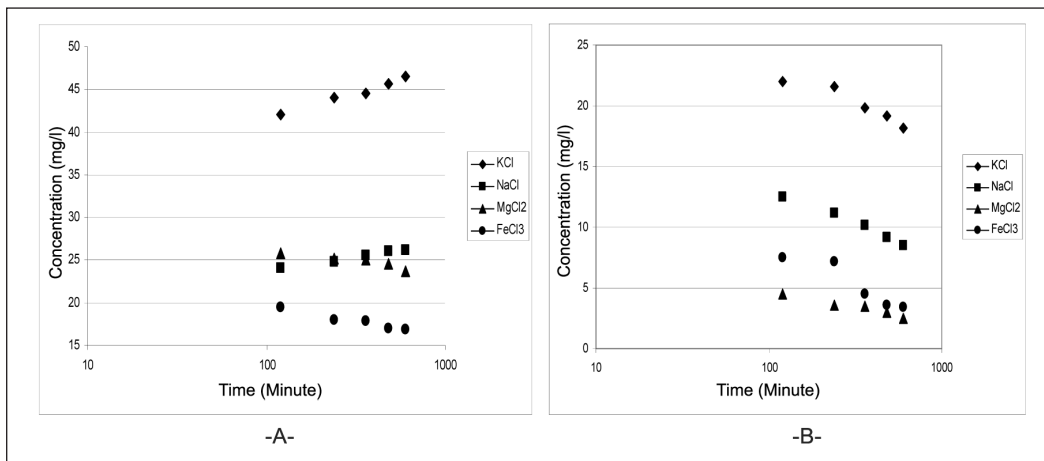


Figure 12- From activated chabazitic tuffs with 0.1 N H<sub>2</sub>SO<sub>4</sub> (A) and with 0.1 N HCl (B) as depend ing on time, Ca<sup>+2</sup> content passing to the solutions.

**Table 2- From activated chabazitic tuffs with 0.1N H<sub>2</sub>SO<sub>4</sub>, as depending on time, Ca<sup>+2</sup> content passing to the solutions**

Time Minute	The cation from chabazitic tuffs passing to the solutions	Solutions (500 ppm)			
		In KCl solution	In NaCl Solution	In MgCl <sub>2</sub> solution	In FeCl <sub>3</sub> Solution
120	Ca <sup>+2</sup> (mgr/l)	42.0	24.0	25.8	19.5
240	Ca <sup>+2</sup> (mgr/l)	44.0	24.8	25.2	18.0
360	Ca <sup>+2</sup> (mgr/l)	44.5	25.5	25.0	17.8
480	Ca <sup>+2</sup> (mgr/l)	45.6	26.0	24.5	17.0
600	Ca <sup>+2</sup> (mgr/l)	46.5	26.2	237.0	16.8



**Table 3- From activated chabazitic tuffs with 0.1N HCl , as depending on time, Ca<sup>+2</sup> content passing to the solutions**

Time Minute	The cations, from chabazitic tuffs passing to the solutions	Prepared Solutions (500 ppm)			
		In KCl solution	In NaCl solution	In MgCl <sub>2</sub> solution	In FeCl <sub>3</sub> Solution
120	Ca <sup>+2</sup> (mgr/l )	22.0	12.5	4.5	7.5
240	Ca <sup>+2</sup> (mgr/l )	216.0	11.2	3.6	7.2
360	Ca <sup>+2</sup> (mgr/l)	19.8	10.2	3.5	4.5
480	Ca <sup>+2</sup> (mgr/l )	19.2	9.2	3.0	3.6
600	Ca <sup>+2</sup> (mgr/l )	18.2	8.5	2.5	3.4

on time. In spite of having become a decreasing of Ca<sup>+2</sup>, K<sup>+1</sup> contents from phillipsitic tuffs activated with 0.1N HCl passing to the FeCl<sub>3</sub> solution, having become a increase of Na<sup>+1</sup> content passing to the FeCl<sub>3</sub> solution were determined (Table 5 and Figure 14).

## DISCUSSIONS

In the light of the experimental results of ion exchange capacity of Sandıklı chabasitic and phillipsitic tuffs, the zeolitic tuffs of the region will be evaluated for healthing and soil improvement in this part. According to existing data, obtained results are debated below.

The agricultural areas of the region are settled on the pyroclastic rocks and/or lacustrine sediments with volcanic ash intercalations. In the investigated area, the volcanic rocks have high concentrations of Cs (11.10 - 88.30 ppm) and Sr (1208.20 - 3246.70 ppm) (Özpinar, 2001). In addition, in the region, cold water contains of Sr about 2.65 mgr and hot water contain of Sr between (4.15-4.75 mgr) (Afşin, 1991). Besides, while the <sup>90</sup>Sr is between 1.22 pCi/l and 2.5 pCi/l in the hot water of the region, it is 0.44 pCi/l in the cold water. After this, Cs and Sr passing from phosphatic organic dungs to the soil and to the vegetables are about 80 mgr/kg and between 25-500 mgr/kg respectively and Sr passing from organic dungs to the soil and vegetables are

about 20 mgr/kg (Mikayilov and Acar, 1998). As a result in soils and vegetables the contents of Cs and Sr increase. After Chernobyl nuclear accident, no any region except east Black Sea, have been investigated in terms of <sup>137</sup>Cs concentration in soils. According to Gür and Yaprak (2003) Gediz Region (western Anatolia) has been contaminated by radioactive elements (<sup>137</sup>Cs and <sup>90</sup>Sr) distributed from the Chernobyl nuclear accident. Like Gediz region, all western Anatolia have been affected by <sup>137</sup>Cs and <sup>90</sup>Sr isotops distributed with air circulations, and <sup>137</sup>Cs and <sup>90</sup>Sr concentration have been increased too much in the environment. In this situation, chabazite and phillipsite may be used to prevent passing of radioactive elements from nature to the environment and biological systems.

Radioactive elements cause important differences on the biological systems. According to the study of Epik and Yaprak (2003) on the leafed forests of the İzmir -Kozaklı region, the <sup>40</sup>K contamination is in excess concentrations. In the investigated area, volcanics are potassic and ultrapotassic in character (Özpinar, 2001). In studied area, it is estimated that <sup>40</sup>K contamination may be too much. As known, the human's body of weight about 70 kg contains about 140 gr K and only the part of 0.03 gr of this content is <sup>40</sup>K. As a result, it is understood that these minerals may be used for improvement of soil.

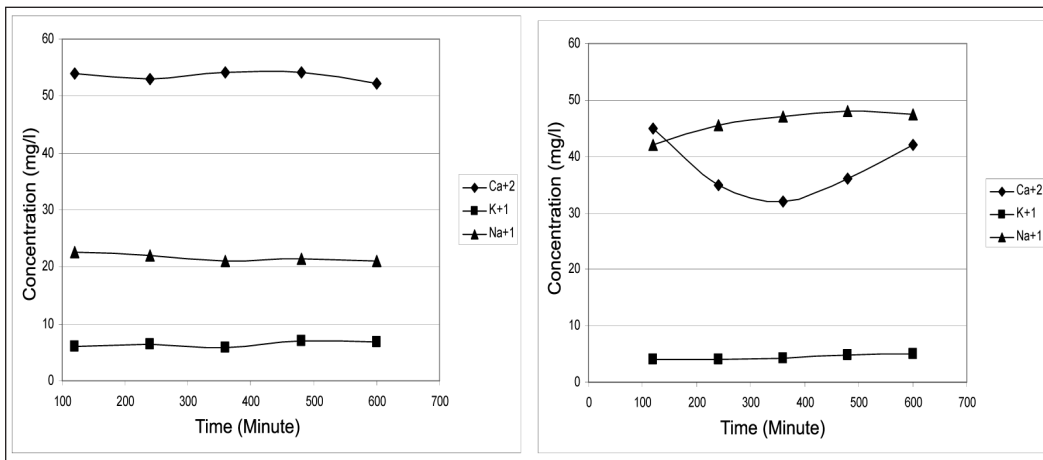


Figure 13- From activated phillipsitic tuffs with 0.1N H<sub>2</sub>SO<sub>4</sub>, as depending on time, Ca<sup>+2</sup>, K<sup>+1</sup> and Na<sup>+1</sup> content passing to the FeCl<sub>3</sub> and MgCl<sub>2</sub> solutions.

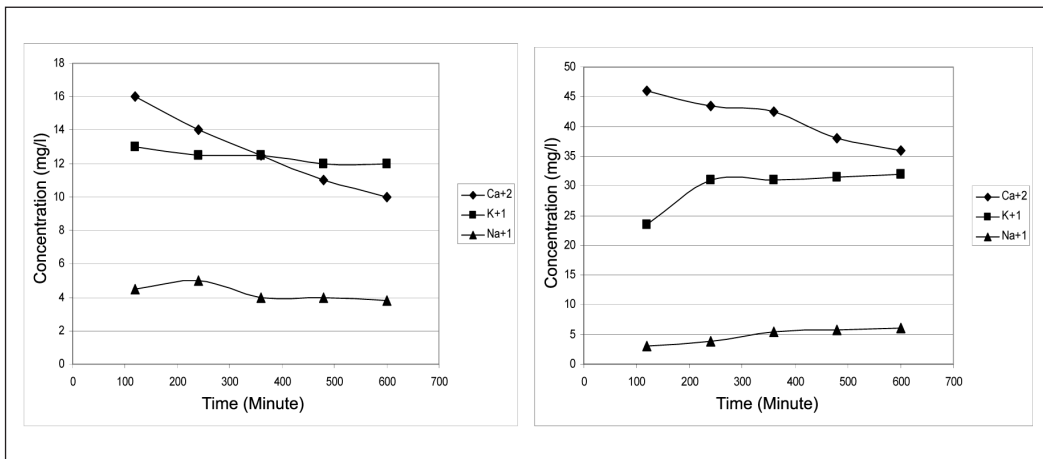


Figure 14- From activated phillipsitic tuffs with 0.1N HCl, as depending on time, (Ca<sup>+2</sup>, K<sup>+1</sup> and Na<sup>+1</sup> contents passing to the FeCl<sub>3</sub> and MgCl<sub>2</sub> solutions.

In Gördes zeolitic rocks, ammonium-exchange capacity were studied by Esenli (2006). According to author, the zeolite contents increased from 0 (non-zeolitic) to about 30-40 wt, % in the rock samples. It is not seen a significant increase on the ammonium-exchange capacity for the group of samples containing 40-80 wt, % of zeolite. But the ammonium-exchange capacity is higher for the samples containing more than 70-80 wt, % of zeolite. Using of nitrogenous manure cause to increase amount of nitrate (NO<sub>3</sub>) and ammonium (NH<sub>4</sub>) in soil and groundwater.

Related to this, the amount of ammonium is too high in the agricultural areas of this region. Because of ammonium exists in the selective series of chabazite, ammonium ions are easily concentrated on chabazite from solutions. As a result by using of the zeolites in agricultural areas, the excess ammonium is removed from soil and prevent ammonium poisoning.

It is important that activated natural zeolites become excessively tendency to the resorption and adsorption of moisture. Because of this fea-

**Table 4- From activated phillipsitic tuffs with 0.1N H<sub>2</sub>SO<sub>4</sub>, as depending on time, Ca<sup>+2</sup>, K<sup>+1</sup> and Na<sup>+1</sup> contents passing to the FeCl<sub>3</sub> and MgCl<sub>2</sub> solutions**

Time Minute	MgCl <sub>2</sub> solution(500 ppm)			FeCl <sub>3</sub> solution (500 ppm)		
	Ca <sup>+2</sup> content, from phillipsite passing to the solution (mgr/l)	K <sup>+1</sup> content from phillipsite passing to the solution (mgr/l)	Na <sup>+1</sup> content from phillipsite passing to the solution (mgr/l)	Ca <sup>+2</sup> content from phillipsite passing to the solution (mgr/l)	K <sup>+1</sup> content from phillipsite passing to the solution (mgr/l)	Na <sup>+1</sup> content from phillipsite passing to the solution (mgr/l)
120	54,0	6,0	22,5	45,0	4,0	42,0
240	53,0	6,5	22,0	35,0	4,0	45,5
360	54.2	5,9	21,0	32,0	4,3	47,0
480	54.1	7,0	21,5	36,0	4,8	48,0
600	52.3	6,8	21,0	42,0	5,0	47,5

**Table 5- 0.1N HCl ile aktifleştirilmiş doğal zeolitten zamana bağlı olarak FeCl<sub>3</sub> ve MgCl<sub>2</sub> çözeltilerine geçen Ca<sup>+2</sup>, K<sup>+1</sup> ve Na<sup>+1</sup> iyonlarının miktarı**

Time Minute	Solution; MgCl <sub>2</sub> (500 ppm)			Solution; FeCl <sub>3</sub> (500 ppm)		
	Ca <sup>+2</sup> content , from phillipsite passing to the solution (mgr/l)	K <sup>+1</sup> content from phillipsite passing to the solution (mgr/l)	Na <sup>+1</sup> content from phillipsite passing to the solution (mgr/l)	Ca <sup>+2</sup> content from phillipsite passing to the solution (mgr/l)	K <sup>+1</sup> content from phillipsite passing to the solution (mgr/l)	Na <sup>+1</sup> content from phillipsite passing to the solution (mgr/l)
120	16,0	13,0	4,5	46,0	23,5	3,0
240	14,0	12,5	5,0	43,5	31,0	3,8
360	12,5	12,5	4,0	42,5	31,0	5,5
480	11,0	12,0	4,0	38,0	31,5	5,7
600	10,0	12,0	3,8	36,0	32,0	6,0

ture, activated natural zeolites may be used as decicant as well. This quality of zeolites makes contribution to the plants development by preserving of the moisture of the soil. In this context, the tuffs of the study area have value of absorption wt % between 13.40% -24.45 % and vol.% between 24.8% -33.17 % (Özpinar, 1998; Özpinar et al., 2002). As resut, for plant development, it is thought that zeolitic tuff of this region will do important contribution.

As it is known that phillipsite contains sodium and potasium ions. Using for soil improvement may cause increasing of the amount of alkali in soil, so in the acidic soils it plays a role of stabilization of pH, and because of this feature they may be used in soil improvements.

In the last years, using of zeolite instead of clay for garbage dumps has increased. It is shown that they may be used to prevent leaking



of harmful ions into the groundwater from the surface. Beside, if they use, they reduce the dirty smells and decrease to cost of making dump.

At Sandıklı and its surrounding area, there are many shelters of cattle and goats. Because of this situation, they disperse dirty smells to the environment. Zeolites can absorb the dirty smells deriving from urine, fecal matter and ammonium. So, zeolitic tuffs may be used for shelter of cattles and goats.

Chabazitic tuffs use in different localities of world for heating and air conditioner of small houses. Compressive strength of zeolitic tuffs are 108 kgf/cm<sup>2</sup> as average (Özpinar, 1998; Özpinar et al., 2002). It may be used for this purpose in the Sandıklı and surroundings settlements.

In study area, because of tuffits are consolidated, it may be used to store fruits and vegetables too. and finally it is satisfied that for this situation can be encouraged by local authority.

## CONCLUSIONS AND SUGGESTIONS

By this study, the results obtained are given below, Sandıklı volcanics are widespreadly exposed at the southern part of Sandıklı and they are represented by lavas of trachyandesitic, phonolitic tephritic, basaltic andesitic, basaltic trachy-nephelinitic, andesitic and dacitic in compositions and thick pyroclastics rocks. Pyroclastic rocks from bottom to top are represented by lapillistone, tuffaceous conglomerate, tuffaceous sandstone, tuffaceous siltstone and tuffaceous mudstone.

The tuffs and altered lavas contain chabazite and phillipsite minerals firstly determined by Özpinar (1998). However, in this paper, investigations on the zeolite occurrences in tuffs have been focused much more. At Selcik village and its surrounding area which is located in the northern part of the investigated area the chabazite

occurrences are found widespreadly in cream coloured tuffs and in the southern part the phillipsite occurrences are found widespreadly in gray, dark gray and brownish coloured tuffs. The tuffs outcropped at Ballık village and its surrounding area, contain chabazite and phillipsite occurrences. Three phillipsite forms were defined. These are potassium-sodium-aluminum-silicate hydrate, potassium-aluminium-silicate hydrate, potassium-calcium-aluminium silicate hydrate.

In tuff specimens purified with heavy liquid, in cream colored tuffs, the amount of chabazite as wt. % are between 29.00 % -58.93 % and in gray, dark gray and brownish colored tuff, the amount of phillipsite as weight % are between 51.53 % - 63.00 %. However, tuffs located at eastern of Soğucak village are found extensively zeolitization which the amount of phillipsite are about 80- 85 %.

From chabazitic tuffs (Selcik tuffs) activated with 0.1 N H<sub>2</sub>SO<sub>4</sub>, as depending on time, Ca<sup>+2</sup> content (mgr/l) has been passed increasingly to the NaCl and KCl solutions and decreasingly to the MgCl<sub>2</sub>, FeCl<sub>3</sub> solutions and also from activated chabazitic tuffs with 0.1 N HCl, depending on time, Ca<sup>+2</sup> (mgr/l) content has been passed decreasingly to the KCl, NaCl, FeCl<sub>3</sub> and MgCl<sub>2</sub> solutions (Table 5 and figure 12 ).

From phillipsitic tuffs activated with 0.1N H<sub>2</sub>SO<sub>4</sub> Ca<sup>+2</sup>, K<sup>+1</sup>, as depending on time, Ca<sup>+2</sup>, K<sup>+1</sup> contents passing to the FeCl<sub>3</sub> solution (500 ppm) have become too much than passing to the MgCl<sub>2</sub> solution (500 ppm). In spite of this, Na<sup>+1</sup> content passing to the MgCl<sub>2</sub> solution have become too much than passing to the FeCl<sub>3</sub> solution. On the other hand, Ca<sup>+2</sup>, K<sup>+1</sup> and Na<sup>+1</sup> contents, from activated phillipsitic tuffs with 0.1N HCl, Ca<sup>+2</sup>, K<sup>+1</sup> and Na<sup>+</sup> contents passing to the MgCl<sub>2</sub> solutions have become a decrease as depending on time. In spite of having become a decreasing of Ca<sup>+2</sup>, K<sup>+1</sup> content from phillipsitic tuffs activated with 0.1N HCl passing to the FeCl<sub>3</sub> solution, having become a increase of Na<sup>+1</sup> con-

tent passing to the FeCl<sub>3</sub> solution were determined.

When we keep in view of ion exchange capacity and selection of the radioactive cations such as <sup>137</sup>Cs, <sup>90</sup>Sr and <sup>40</sup>K of chabazite and phillipsite tuffs may be used for improvement of soil, stabilization of pH of acidic soil and for prevent to pass by radioactive element from nature to environment and biological systems. Because of activated natural zeolites become excessively tendency to the resorption and adsorption of moisture and for the plants development will do contribution, activated natural zeolitic tuffs may be used as decicant. Because of adsorption of ammonium smells arised from urine and fecal matter, it is thought that zeolitic tuffs may be used to separation of the methane gas, from the other gases. Besides, it is believed that they are possible to use as building stone for heating and air conditioner of small houses and shelter of cattles and goats.

In order to prevent the leaking harmful ions into the groundwater from surface and to reduce dirty smells, it could be possible to make low cost garbage dumps by using the zeolitic tuffs of the region .

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