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AN IMPORTANT CHABASITE OCCURRENCE IN CENTRAL ANATOLIA AND ITS MINERALOGICAL FEATURES

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ABSTRACT.- The Lower - Middle Miocene Aktepe Formation cropping out to the south of Ankara (Central Anatolia) is comprised of volcano - sedimentary lacustrine deposits. In the formation mainly three zeolitic tuffaceous layers including dominant chabasite were determined. Based on the data obtained from XRD and SEM investigations, it was determined that the authigenic zeolite minerals are chabasite, erionite and clinoptilolite, and minor smectite in some samples. Where the clinoptilolite is dominant, at a location, it has been observed that K-feldspar enters into the mineralogical composition. The main mineral assemblages in zeolitic tuffs are determined as "chabasite + erionite + clinoptilolite" and "chabasite + erionite + clinoptilolite + K-feldspar".The first data obtained points out that the Aktepe Formation has deposited in a saline - alkaline lacustrine environment. It can be said that, the zeolitic tuff occurrences in which chabasite is abundantly present, has economical potential.

Key words: Chabasite, zeolite, Central Anatolia, Lower - Middle Miocene, volcano sedimentary rocks.

INTRODUCTION

In Central Anatolia, according to the studies carried out by Temel and Gündoğdu (1996) around Cappadocia, chabasite mineral is found in zeolitic tuffs which are known to be widespread in this region. The first chabasite occurrence that have economical potential, however, has been found in Lower - Middle Miocene volcanosedimentary - lacustrine deposits to the 80 km south of Ankara (Figure 1) in the scope of a project realized by MTA in Central Anatolia.

The zeolite occurrences located in the study area corresponds to the "closed basin zeolites" proposed by Sheppard and Simandi (1999). In this region, during the previous geological investigations on the basis of the formations (Aktepe Formation), it has ben stated that the lacustrine deposits contained volcanic intercalations and various tuff layers (Uğuz et al., 1999). However, no information on the mineralogical compositions of the tuffs and zeolite occurrences was given in this study (Uğuz et al., 1999).

During the studies explained in this paper, pre-sence of zeolitic occurrences and their mineralogical compositions have been revealed for the first time. The field work carried out on the Ak-tepe formation cropping out near Akviran-çarsak Village, which is comprised of a volcanosedimentary lacustrine sequence including three main zeolitic tuff layers. The distance between the tuff layers, of which thickness is about 20 cm - 1.5 m, varies between 1.5 - 4 m. The dips of the beds vary (25°-90°) based on tectonic effects. The samples collected from these beds have been studied by using the XRD and SEM methods and the mineralogical and textural features of the zeolite minerals (chabasite, erionite, clinoptilolite) have been revealed.

TECTONIC SETTING

The study area is located in about 80 km south of Ankara on a subduction zone separating the deposits of active and passive continental margin, called Sakarya continent and Central Anatolian Metamorphic Massifs (Görür et al., 1984; Dellaloğlu et al., 2001; Figure 2). The basement rocks cropping out in Central Anatolia, in general, are defined as a micro-plate surrounded by branches of Neo-Tethys during Mesosoic - Paleocene period (Şengör et al., 1984).

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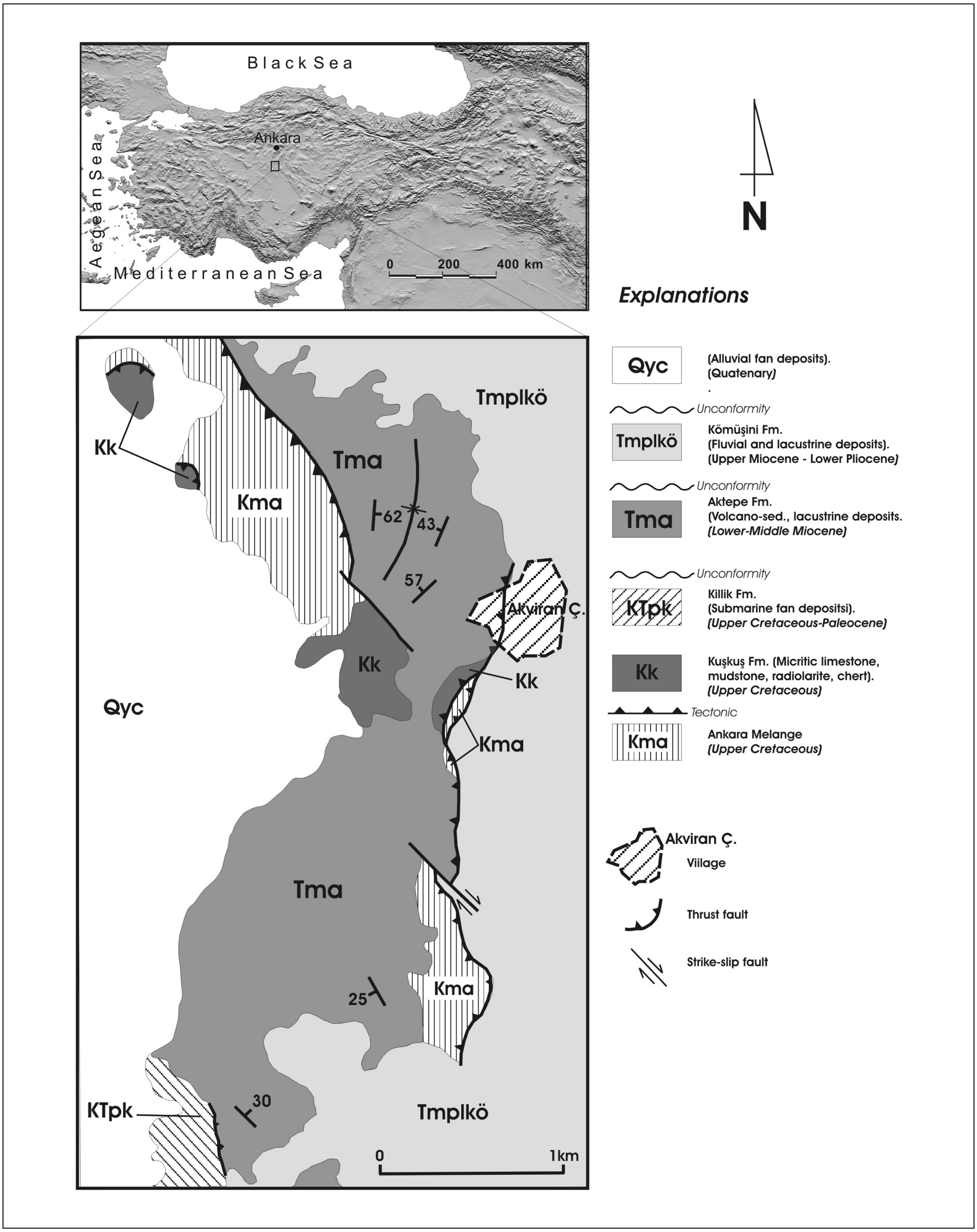

Figure 1- Location and simplified geological map of the study area (after Uğuz et al., 1999).

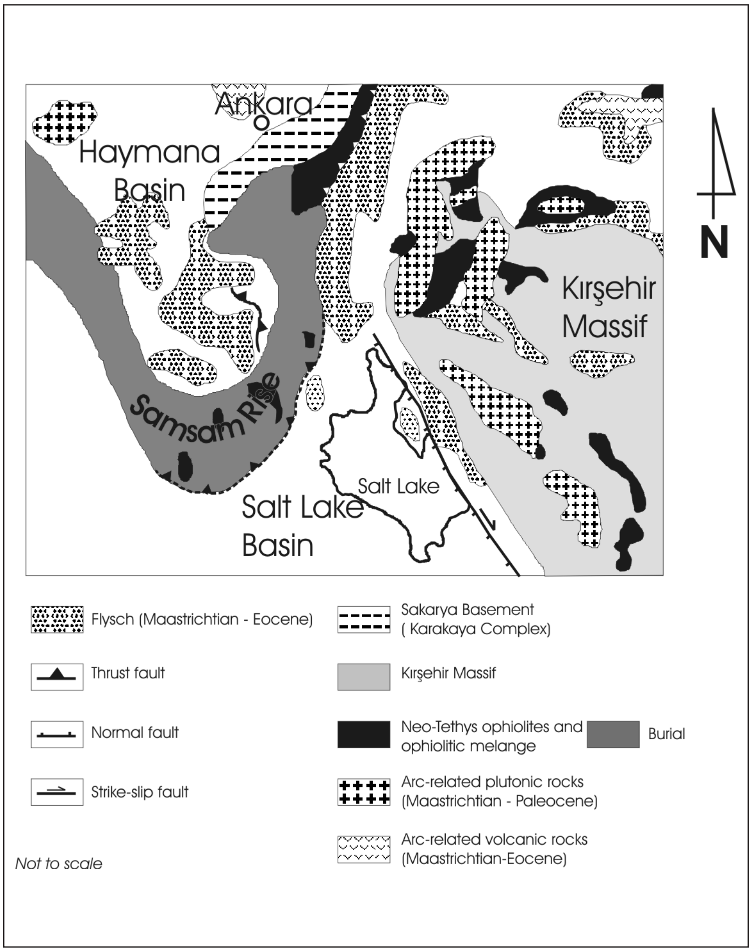

Figure 2- Simplified geological map of the Lake Tuz Basin and the sur rounding regions (Görür et al., 1984).

As a result of the continental collision (Kırşehir Block - Sakarya Continent) during Late Maastrictian - Late Paleocene, Haymana and Salt Lake basins have formed, on the other hand, the ophiolitic melange known as Ankara Melange has emplaced. This ophiolitic melange, which separates the Haymana and Salt Lake basins with a structural rise namely Samsam rise (Görür et al., 1984) on which the study area has been developed (Figure 2).

While the lacustrine deposits are comprised of Neogene clastics and evaporites overlying the Eocene marine deposits and the ophiolitic melange, in certain regions have volcanic products as well. The volcanic series which are comprised of tuff and lavas in general, are laterally transitive to lacustrine deposits mainly dominated by carbonates and clastics. The ophiolitic melange of the Samsam Rise and the overlying volcanic and / or volcanoclastics are widespreadly observed, and at the basement, marine units of the Haymana Basin take place.

GEOLOGICAL CHARACTERISTICS

The formation in which zeolitic tuff occurrences are included in the study area is the Lower - Middle Miocene Aktepe formation (Uğuz et al., 1999). This is a widespread formation in Central Anatolia and typically crops out around Çankırı where it is called Hançılı Formation by Akyürek et al. (1984).

Aktepe formation is stratigraphically located on the Ankara Melange, however, it is observed that Ankara Melange tectonically overlies Aktepe Formation in the study area. The Upper Miocene -Lower Pliocene terrestrial deposits of the Kömüşini Formation (Uğuz et al., 1999) unconformably overlies the Aktepe formation (Figure 1).

Aktepe formation is a volcano - sedimentary sequence made up of siltstone, mudstone, bituminous shale, zeolitic siltstone and zeolites. These series corresponds to a lacustrine depositional environment that has developed during Lower - Middle Miocene and is observed in relation to the Karacadağ Volcanics comprising basaltic - andesitic lava, tuffs and agglomerates (Uğuz et al., 1999).

In the study area, mainly three different zeolitic tuff layers were differentiated: layer 1: average thickness= 40 cm, layer 2: average thickness= 65 cm and layer 3: average thickness= 80 cm (Figure 3). Chabasite bearing zeolitic tuff lenses of 10 - 20 cm thick in average accompanying these layers also exist in the area.

METHODOLOGY

For mineralogical studies, samples were collected from three tuff layers as well as the other lithological units.

The samples selected are outcrop, trench and core samples. On these samples XRD and SEM analyses were carried out and the results were compared.

The mineralogical compositions of the samples were first determined at the XRD Laboratory (Philips, PW 1830: Cu-K , 30 k$_\alpha$V, 40mA,

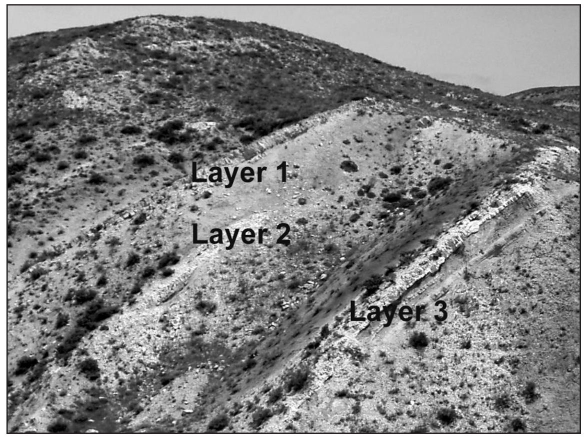

Figure 3- Zeolitic tuff layers bearing chabasite (from older to younger: Layer 3, Layer 2 and Layer 1).

2 θ :2.5°-70°, 6°/dk.) of the Mineralogy - Petrography Laboratory of MTA, later on, the same samples were investigated at the SEM Laboratory of the Hacettepe University (Zeiss, EVO 50-EP: scanning conditions are shown on the photographs).

During the SEM investigations especially the textural features of the samples were revealed as well as their mineralogical contents.

MINERALOGY

XRD INVESTIGATIONS

Whole rock XRD analyses of the samples were performed in order to determine the mineralogical compositions of the zeolitic tuffs. When notice to the mineralogical compositions of the representative samples given in table 1, it can be seen that the dominant zeolite mineral is chabasite. Presence of the erionite and clinoptilolite at various amounts indicate the existence of the "chabasite + erionite + clinoptilolite" paragenesis. Glassy material (volcanic glass) is mostly observed in accompanying to this assemblage. It can be said that the amounts of the minerals vary respectively depending on layers and locations, and that the amount of the chabasite is sufficient to be evaluated as an industrial raw material, and finally that the erionite is in less amounts in the-

Table 1- Mineralogical compositions according to XRD investigations.

Sample No	Layer No	Thickness (cm)	Chabasite	Erionite	Clinoptilolite	Smectite	Amorphous material
GA-158	2	60	dominant	very few	-	-	very few
GA-159	3	65	dominant	very few	-	very few	very few
GA-188*	3	65	dominant	-	-	-	-
GA-192	2	60	dominant	very few	very few	-	very few
GA-193	2	50	dominant	very few	few	-	-
GA-197	2	60	dominant	-	few	-	very few
GA-199	2	150	less	very few	dominant	-	few
GA-200	3	100	dominant	few	very few	-	few
GA-202	1	55	dominant	very few	very few	-	few

GA-188 is core sample. Its thickness is 65 cm, and is taken from a depth of 32 m.

assemblage and clinoptilolite is dominant mineral in only one sample.

By the XRD analysis of the sample taken from Layer 1 (GA-202: Layer 1, Figure 4), it was seen that the zeolite mineral is dominantly chabasite and less amounts of erionite and clinoptilolite are accompanied to the chabasite (Figure 5). Very little amount of amorphous materials were also observed as relict material (Table 1). Thickness of the Layer 1 which is stratigraphically at the top varies betwen 20 - 60 cm.

When the mineralogical composition of the 65 cm thick layer 2 (Figure 6), is investigated according to the results of XRD analyses, it was seen that the dominant zeolite mineral was chabasite in many samples (GA-158, GA-192, GA-193, GA-197) collected from different locations of this layer, and erionite, clinoptilolite and amorphous material are included in different amounts (Table 1, Figure 7a, b, c, d). To the north of the area the thickness of the layer increases from 60 cm to 150 cm; similarly, the mineralogical composition also changes (GA-199, Table 1, Figure 7e). Clinoptilolite is dominant zeolite in sample no. GA-199, and in XRD analyses, reflections of chabasite minerals can not be observed clearly.

The stratigraphically lowest Layer 3 (Figure 3, 4 and 8) is a 65 - 100 cm thick layer where it crops out, and chabasite is the dominant zeolite mineral (GA-159, GA-188, GA-200) in this zeolitic tuff layer. According to the XRD analysis of the samples collected from the surface, erionite, clinoptilolite and amorphous materials (volcanic glass) are presented in minor amounts (Table 1, Figure 9a, b). The XRD anaysis of the core sample (GA-188: thickness=65 cm) taken from this layer does not reflect the other components except chabasite.

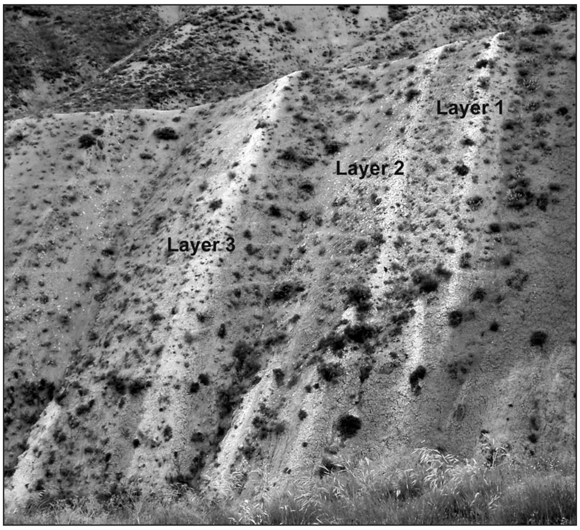

Figure 4- Chabasite bearing upstanding zeolitic tuff layers (GA-202: chabasite dominant; collected from layer 1; thickness: 55 cm)

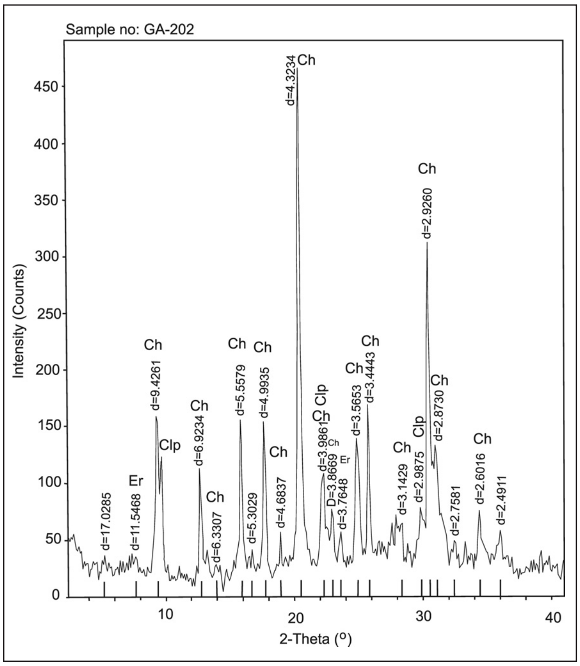

Figure 5- XRD diffractogram of sample no. GA-202; Ch: chabasite, Clp: clinoptilolite, Er: erionite.

Figure 6- Zeolitic tuff layer bearing abundant chabasite (Layer 2, GA-197: Chabasite dominant, thickness of chabasite: 65 cm).

SEM INVESTIGATIONS

The components, crystal sizes, morphologies and grain relations of the zeolitic tuff samples of which mineralogical components were determined by XRD analyses have been defined by scanning electron microscope (SEM).

The minerals taking place in Table 1 and observed through SEM investigations in the samples of which mineral compositions were determined by XRD analyses are given in table 2.

Chabasite

Chabasite is the dominant zeolite mineral found in all of the samples studied. Its rhombohedral grain sizes varying betwen 0.5 - 4 μm are typical (Figure 10). Especially the crystallizations developed in between the pores and voids are eye - catching; besides, local aggregations or clusterings of chabasite crystals are also observed (Figure 11a, b, c). Well developed twinnings of the minerals in such occurrences are common.

Erionite

In the SEM studies, it was seen that erionite is the zeolite mineral which accompanies the chabasite mineral in all samples. While mostly observed as bundles of acicular crystals (Figure 12), erionite crystals in form spicules or filaments can also be observed. Its crystal size may reach up to 15 - 20 μm.

According to XRD analyses, it occurs in little amounts or does not exist as in the sampes numbered GA-188 and GA-197. SEM studies, however, reveal the existence of erionite in both samples (Figures 11c, 13). Failure in determination of erionite in these samples may be explained by its minor ratio in the mineralogical composition.

Clinoptilolite

Clinoptilolite minerals are found in the forms of well developed laminated crystals, inwhich crystal size may reach up to 50 μm. Although it is not observed in all of the samples, when presented, it accompanies to the chabasite and erionite minerals.

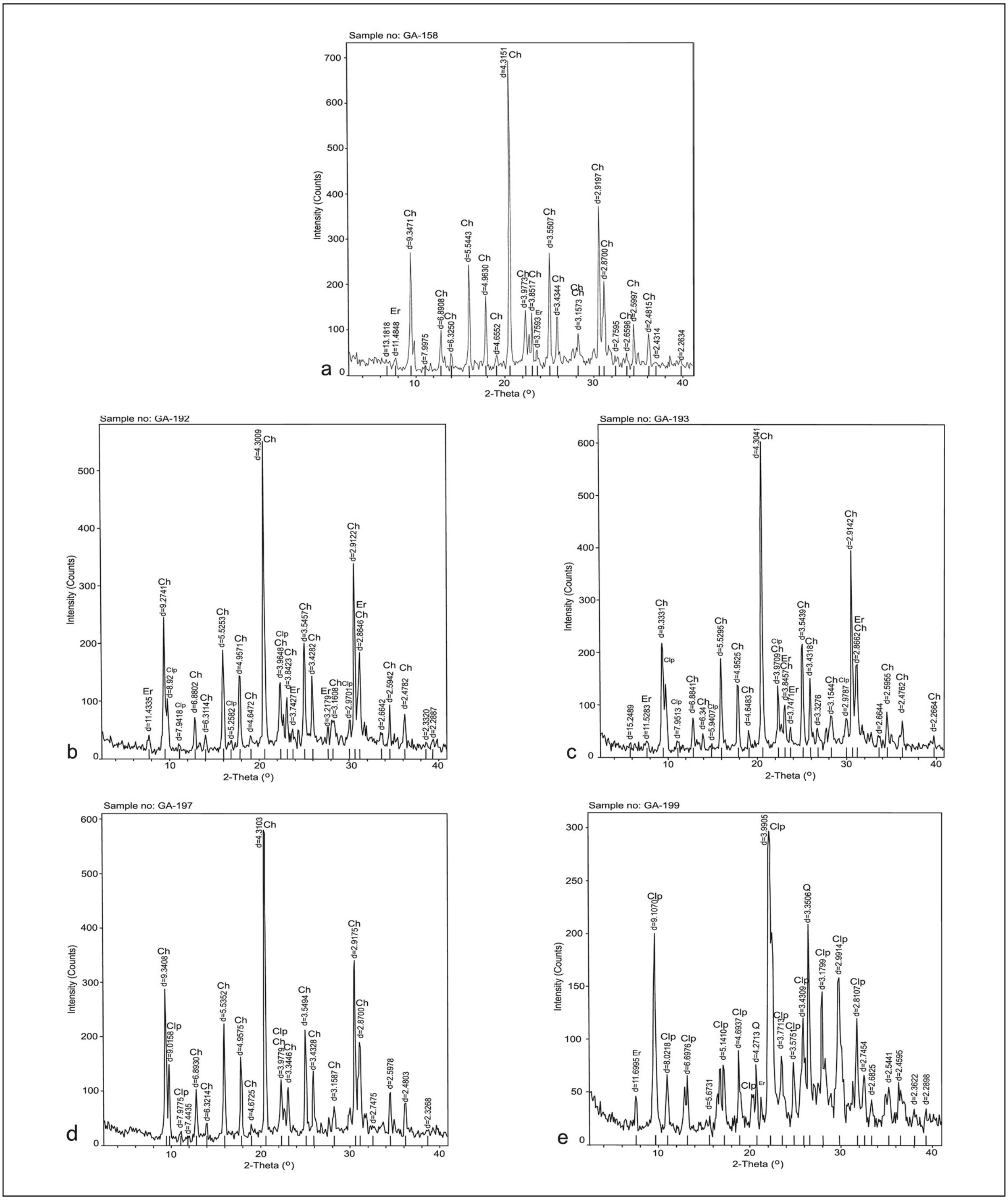

Figure 7- XRD diffractograms of samples taken from Layer 2; Ch: chabasite, Er: Erionite, Clp:Clinoptilolite Q: Quartz; (a: GA-158), (b: GA-192), (c: GA-193), (d: GA-197), (e: GA-199).

Table 2- Mineralogical compositions according to SEM investigations

Sample No	Laye r No	Thickness (cm)	Chaba site	Erionit e	Clinoptilolite	Smectit e	Amorph ousf material	K-feldspar
GA-158	2	60	+	+	+	-	+	-
GA-159	3	65	+	+	-	+	+	-
GA-188*	3	65	+	+	-	-	+	-
GA-192	2	60	+	+	+	-	+	-
GA-193	2	50	+	+	-	-	+	-
GA-197	2	60	+	+	+	-	+	-
GA-199	2	150	+	+	+	-	+	+
GA-200	3	100	+	+	+	-	+	-
GA-202	1	55	+	+	+	-	+	-

GA-188 is core sample. Its thickness is 65 cm, and is taken from a depth of 32 m.

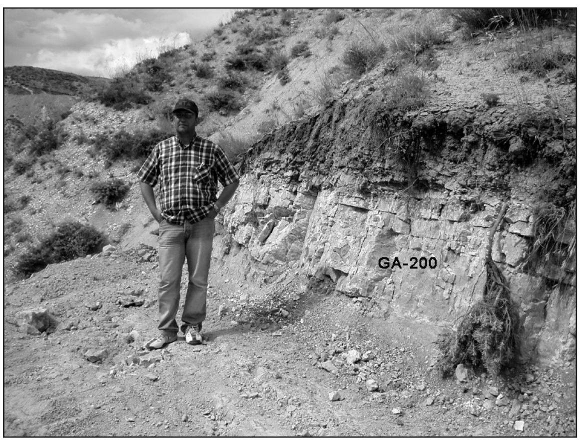

Figure 8- The stratigraphically lowermost zeolitic tuff layer (Layer 3, GA-200, chabasite dominant, thickness 100 cm).

It is mostly observed in less amounts in most of the samples, only in sample no. GA-199, while the chabasite is in less amount, clinoptilolite is the dominant zeolite mineral.

It forms the "chabasite+erionite+clinoptilolite" assemblage when presented in rocks (Figure 14).

K-feldspar

K-feldispat is observed in one of the samples (GA-199) taken from chabasite bearing zeolitic tuff layers. Well developed K-feldspar rhombohedrals are typical. Grain size varies between 1-15 µm (Figure 15).

In sample GA-199 where the "K-feldspar + clinoptilolite + erionite + chabasite" assemblage is observed, and the amount of chabasite is less while clinoptilolite is dominant according to XRD analysis.

Volcanic glass and clay minerals

Volcanic glass is abundant in all samples and it is a starting material for crystallization. It displays reflections of amorphous materials in XRD analyses and are found less.

Smectite is a clay mineral observed in a few samples of chabasite bearing zeolitic tuffs as minor minerals through XRD analyses. In SEM investigations well developed crystals of smectite are not found.

PARAGENETIC RELATIONS

In the studies made by Eyde et al. (1987) on chabasite bearing zeolitic tuffs in Bowie, it has been especially pointed out that the paragenetic relations between zeolites and smectites (Hay, 1966) are different than the zeolite occurrences in saline, alkaline lakes defined by Sheppard and

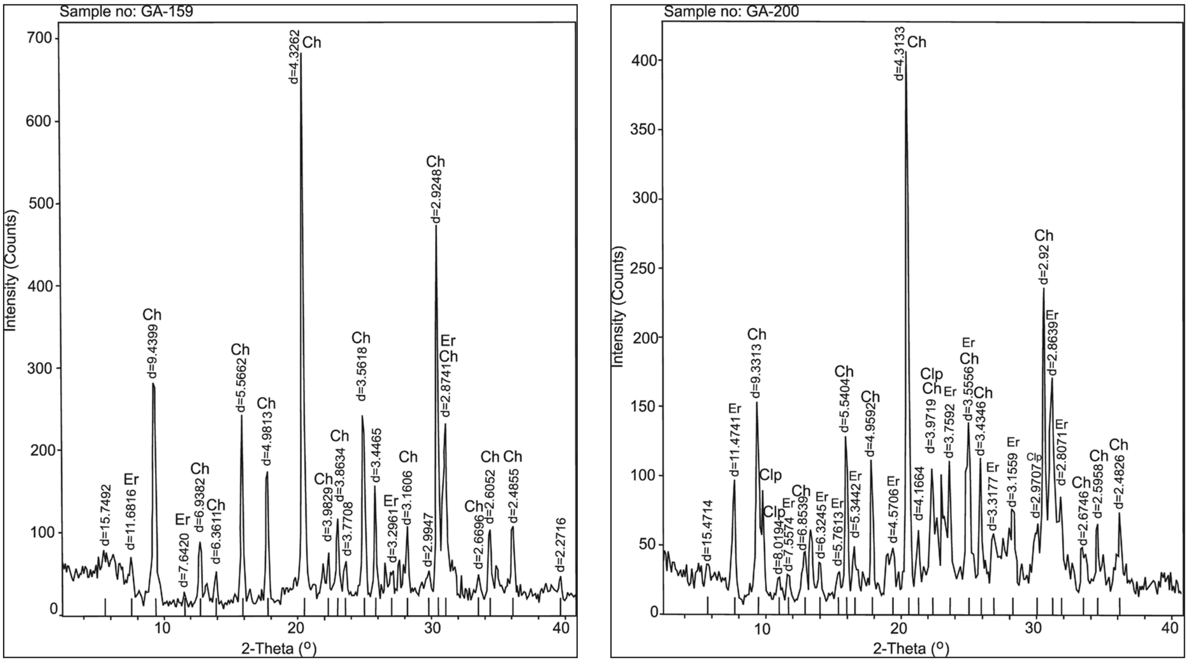

Figure 9- XRD diffractograms of the samples taken from Layer 3; Ch: chabasite, Er: Erionite, Clp:Clinoptilolite Q: Quartz; (a: GA-159), (b: GA-200).

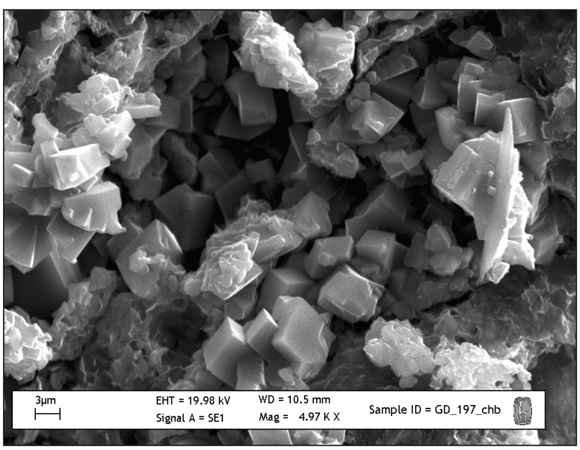

Figure 10- Rhombohedric chabazite minerals (GA-197, Layer 2).

Gude (1968, 1973). The SEM investigations made during this study showed that, here, smectite is not the first forming authigenic mineral (Eyde et al., 1987). It has been expressed that, in Bowie, the first forming authigenic minerals are chabasite and erionite and the latter is observed on poly - crystalline chabasite laminates and most possibly formed after chabasite. Chabasite and erionite minerals taking place in partly or wholly altered zeolites are observed to be coated by smectite, on the other hand, the clinoptilolite minerals crystallized after chabasite and erionite are not coated by smectite, therefore, it can be claimed that they formed after smectite and the other zeolites (Eyde et al., 1987).

The SEM investigations of the samples collected from the study area display paragenetic relations similar to that in Bowie zeolites. It has been observed that zeolite minerals are formed by the alteration of silicic volcanic glass, and many samples include relict silicic glass in less amounts. In only one sample, it has been thought that smectite, which is found in less amounts, is not the first forming authigenic mineral as it was in Bowie. The acicular erionite crystals developed on chabasite minerals imply that probably

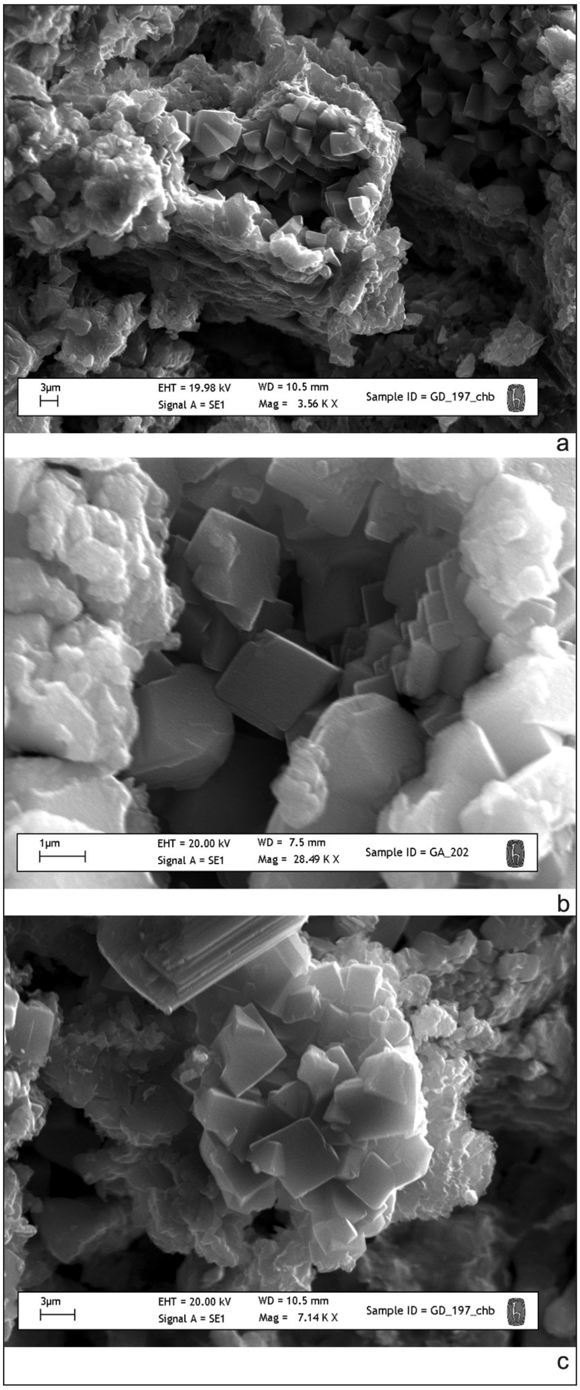

Figure 11- Rhombohedral chabasite developed in pores and voids (a: GA-197-Layer 2; b: GA-202- Layer 1), aggregations formed by chabasite minerals having well developed twinnings (c: GA-197-Layer 2).

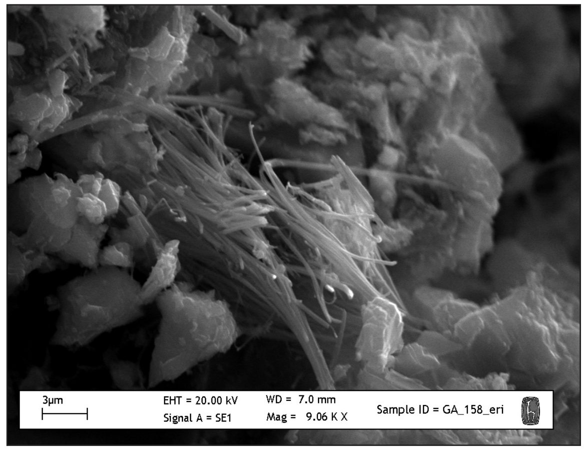

Figure 12- Bundles of acicular erionite minerals (GA-158).

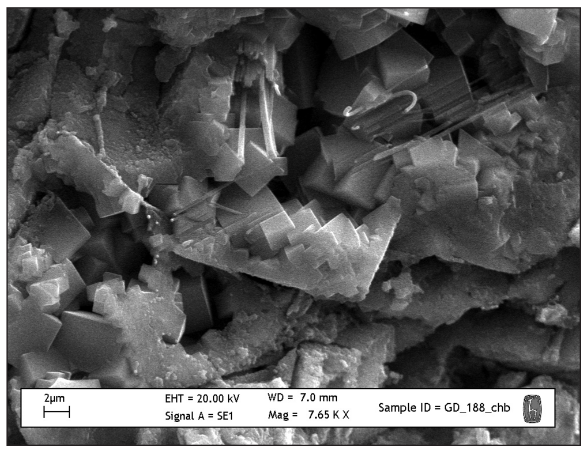

Figure 13- Acicular erionite crystals developed on chabasite minerals (GA-188).

chabasite formed before (Figure 13). In Figure 14, it has been understood that, the clinoptilolite developed at the center of a void, of which inner walls are coated by chabasite, formed before clinoptilolite.

In the study area, in some samples where "chabasite + erionite + clinoptilolite" assemblage is observed, it was thought that the order of formation of zeolite minerals probably is, as it was in Bowie, (1) chabasite, (2) erionite, and (3) clinoptilolite (Figure 14, 16).

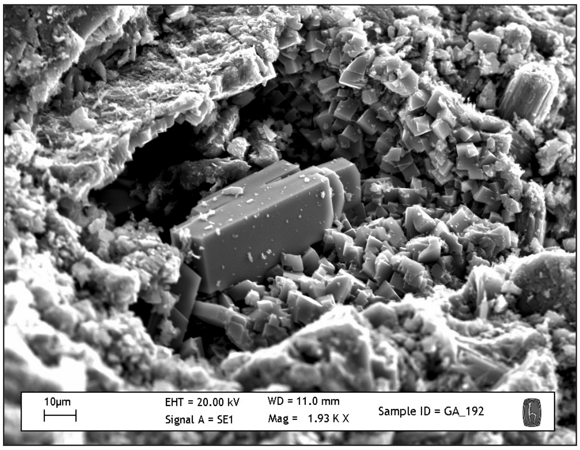

Figure 14- Well developed laminated clinoptilolite minerals and "chabasite + erionite + clinop tilolite" assemblage (GA-192).

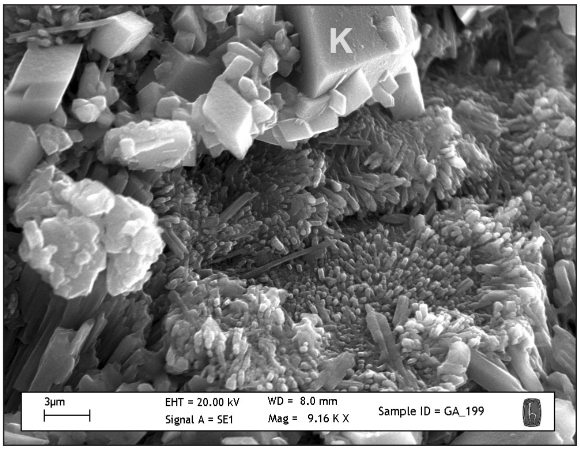

Figure 15- Well developed K-feldspar rhomboids found together with erionite and chabasite (GA-199).

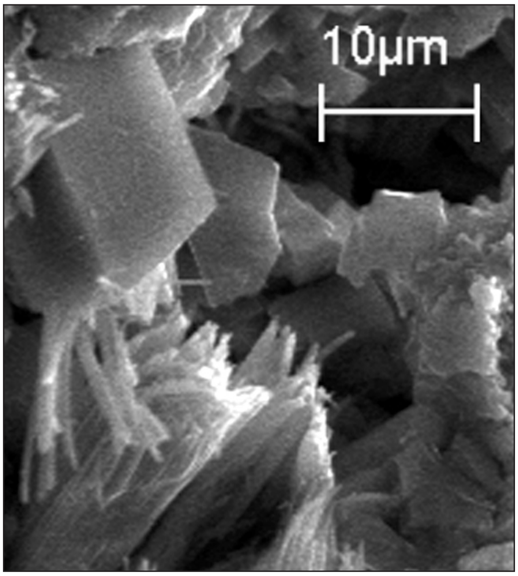

Figure 16- Erionite bundles developed after the formation of chabasite and clinoptilolite that have formed later (GA-197).

DISCUSSION AND CONCLUSIONS

During this study which reflects some part of the data collected during a project to search the industrial raw materials implemented by the General Directorate of MTA, mineralogical findings on some important chabasite occurrences in Central Anatolia were presented.

In the context of the project, it has been determined that the chabasite mineral which has importance for its economical value and areas of use, shows an economical potential in the study area after the Bowie field where the most of the production in the world for chabasite was made. Such zeolite occurrences especially have close relations with economical evaporitic minerals such as borates and trona and since they can give hints on the formation conditions, have great special importance.

According to studies made by Eyde et al. (1987) in Bowie field, paragenetic series of authigenic minerals can provide information on the salinity and alkalinity of the lake water. In the model put forward for Bowie field, it was claimed that when the first volcanic ash is deposited, the lake water is too much alkaline for the formation of smectite, for this reason, before the dissolving of silicic glass, crystallization of chabasite and clinoptilolite took place (Eyde et al., 1987).

In sections where alkalinity and salinity dropped, smectite was formed and later on, upon reaching to the same alkalinity and salinity conditions clinoptilolite was crystallized (Eyde et al., 1987).

In most of the samples collected from the study area chabasite is dominant which indicates that, as in the case of Bowie, the medium here is alkaline and saline. The minor amount of chabasite in "K-feldspar + clinoptilolite + erionite + chabasite" assemblage determined in one sample collected from the north of the study area can be explained by an increasing in the alkalinity in these sections. Detailed investigation of K-feldspar mineral, however, and study of its extension and origin will conclude this assessment.

Zeolites which are mentioned above and are the subjects of this paper, have close relations with the formation of the economical evaporitic mineral beds located in boron basins in Western Anatolia and Beypazarı trona basin in Central Anatolia.

Helvacı et al. (1983) established the relation between the borate minerals and authigenic silicates in Late Miocene intracontinental basins in the northeastern Mediterranean. During this project carried out in the Bigadiç, Sultançayırı, Kestelek, Emet and Kırka basins which are the productive borate basins, the tuffs are found together with borates as intercalations and rich in authigenic silicate minerals such as zeolites, K-feldspar and opal-CT. In borate basins, presence of evaporites themselves and authigenic silicate minerals such as clinoptilolite, analcime, K-feldspar indicate the prevalence of saline - alkaline conditions (Helvacı et al., 1993).

During the study on zeolites in the lacustrine Neogene basins bearing borate in Western Anatolia (Bigadiç, Emet, Kırka basins), paragenesis of clinoptilolite - dominant mineral have been determined, inexistence of silica -rich sodic zeolites (mordenite, erionite, chabasite and philipsite) in this field has also been determined and therefore the zeolite occurrences correspond to saline lacustrine basins (Gündoğdu et al., 1996). Although, it was indicated that, such sodic zeolites occur in the Cenozoic formations like Lake Tecoba, Barstow and Big Sandy (Western USA) mostly together with clinptilolite and these are said to be in important amounts in saline - alkaline lacustrine deposits (Lake Tecoba) which include trona and gaylussite (Sheppard and Gude 1968, 1969, 1973; Surdam and Sheppard 1978; Hay 1978).

Gündoğdu et al. (1996) explain the reasons why silica rich sodic zeolites and trona did not occur in the basin during the presence of non - alkaline conditions and the low activity of sodium in the lake water (Wagon Bed and Chalk Hills Formations; Boles and Surdam, 1979; Sheppard, 1991).

Kırka, Emet and Bigadiç basins and Lake Tecoba where trona beds are located and in Beypazarı basin, during the diagenetical transfer of rhyolitic glass to smectite and clinoptilolite, very important chemical changes do occur; inside the pore solution, together with the Na, K and Mg ions, concentrations of the elements such as B and Li increase (Gündoğdu et al., 1996). During the compaction of the pyroclastics, pore solutions preserved in brine are added to lake waters and consequently, under suitable depositional conditions, evaporitic mineral occurrences in these basins are observed (Gündoğdu et al., 1996).

During the studies in the Beypazarı trona bed, extensive zeolitization, dolomitization and chloritization were observed in trona bed and it was determined that the accompanying rocks and tuff fractions were dominantly zeolites such as analcime, waikerite, natrolite and clinoptilolite (Helvacı, 1998). As for the source of the occurrence of trona, weathering of the granites and Paleocene - Cretaceous volcanics are given; extraction of extensive tuffs are shown to be the main resource for the trona and the other sodium carbonate salts (Helvacı, 1998).

The researches mentioned above show that occurrence of the evaporite mineral beds and the zeolitization ocurred in the same setting as to be closely related. Salinity and alkalinity in the closed lake basins are important factors as well.

According to the mineralogical findings presented in this paper, in the formation of the zeolites (chabasite, erionite and clinoprilolite) taking place in the Aktepe Formation, the origin material is the glassy tuff that have deposited in a lacustrine environment. It was observed that, in many samples the pores or the voids have been filled by zeolite minerals (Figs. 11a, b, 14). This situation is especially typical with chabasite mineral and means that zeolite minerals have been crystallized by the dissolution of the volcanic glass by alkaline - saline pore water during the sedimentation process.

The zeolite occurrences located in the Aktepe Formation, correspond with the "Closed - Basin Zeolites" (Sheppard and Simandi, 1999) by their lithological, mineralogical and the other geological characteristics and their depositional environment has the characteristics of saline - alkaline lacustrine basins.

With these qualifications and upon the detailed studies to be realized in future, Aktepe Formation is going to gain importance for eveporitic mineral beds such as borates and trona.

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