

ZEOLITES AND COEXISTING AUTHIGENIC MINERALS IN MIOCENE TUFFS OF THE ALAÇATI (ÇEŞME) AREA, TURKEY

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Abstract—The zeolites and coexisting minerals of the silicic vitric tuffs in the Alaçatı (Çeşme) area, west of İzmir (Turkey), were studied.ordenite is the most abundant zeolite in tuffs of the Alaçatı area and usually coexists with clinoptilolite-heulandite, smectite and calcite. Opal-CT was identified by means of its crystal morphology and EDX spectrum. Scanning electron microscopy (SEM) revealed the relative age relationships between the zeolites and coexisting minerals, namely mordenite, clinoptilolite-heulandite, smectite, calcite, and, in addition, opal-CT. Smectite consistently crystallized earlier than any of the zeolites, and it occasionally coats the outer walls of some of the vitric material. The zeolites are commonly located on the smectite, although some mordenites were observed to be in direct contact with glass shards that lacked a smectite coating. Clinoptilolite-heulandite formed after smectite and before mordenite. Opal-CT is seen to postdate both smectite and needle-shaped mordenite. Calcite was probably the latest mineral to crystallize in the Alaçatı tuffs. The zeolites in the tuffs of the Alaçatı area formed by dissolution of silicic vitric tuffs by Na- and Ca-rich thermal waters which passed through the fracture zone. The appearance of zeolites together with smectite along this zone may be attributed to a semi-open system which subdivided into smaller closed systems. Small changes in the pH and chemical composition of the thermal waters during alteration produced the corrosion effects observed by SEM. Small amounts of clinoptilolite-heulandite were corroded prior to crystallization of coexisting mordenite. The different compositions of the thermal waters were probably inherited from water that resulted from mixing of thermal and groundwaters.

Key Words—Alaçatı, Calcite, Clinoptilolite-heulandite, Geothermal, Miocene, Mordenite, Turkey, Zeolite.

INTRODUCTION

Zeolites are the common authigenic silicate minerals reported in sedimentary deposits, especially those that originally contained volcanic glass (Hay, 1966). The most common zeolites formed from silicic glass in saline, alkaline environments are phillipsite, clinoptilolite and erionite; less common are chabazite and mordenite (Hay, 1978). There are some cases, in hydrothermal settings, where mordenite was found to be the dominant zeolitic phase as an alteration product (Kitsopoulos, 1997; Pe-Piper, 2000). An example of mordenite formation has been noted by Pe-Piper and Tsolis-Katagas (1991) in the Miocene rhyolitic tuffs at Samos Island, Greece. This mordenite formed by hydrothermal circulation of alkaline lake waters, rich in Ca and K, through the volcanic pile. Mordenite commonly occurs within active geothermal areas as one of the earliest mineral-formed zeolites (Honda and Muffler, 1970; Kristmannsdottir and Tomasson, 1978). Its formation temperature is known to range from ~60 to

160°C (Mas *et al.*, 2000). Likewise, mordenite and clinoptilolite occur in the lower-*T* (60–110°C) parts of some active or recently active geothermal systems elsewhere in the Taupo Volcanic Zone. The main fluid in these systems is weakly saline (alkali-chloride) water, heated by geothermal activity. The formation of mordenite and clinoptilolite, reported by Brathwaite (2003), in the Ngakuru area in the Taupo Volcanic Zone (TVZ), originated from reaction of glass-rich tuff with groundwater-diluted, alkali-chloride water of geothermal origin.

The known zeolite deposits of Turkey were deposited in lacustrine environments. All of these deposits are associated with clay minerals, borates, carbonates and soda minerals. They are also found in close association with lignite-bearing lacustrine rocks and evaporate. For example, the zeolite minerals are found with borates, carbonates and clays in the Kırka (Yalçın, 1988), Emet (Yalçın and Gündoğdu, 1987) and Bigadic (Gündoğdu *et al.*, 1989; Helvacı, 1995) areas. In the Gördes (Esenli, 1993) and Yozgat (Yalçın *et al.*, 1997) regions, zeolites coexist with carbonate and clay minerals and they are interbedded with coal horizons. All of these deposits are rich in clinoptilolite or heulandite, while mordenite is almost absent.

The first mordenite occurrence in the Alaçatı tuffs was discovered by Kaçmaz (2001). The mineralogical

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composition of all tuff samples, as determined by XRD analysis, was reported by Kaçmaz and Köktürk (2004) and zeolite minerals were found in only seven samples out of 40. Those authors suggested that zeolites in tuffs of the Alaçatı area were formed by dissolution of silicic vitric tuffs by thermal waters.

Following a preliminary study, the present study aims to characterize the authigenic minerals and their paragenetic relationships and to reveal the factors controlling the formation of the zeolites and coexisting minerals in the Alaçatı tuffs.

GEOLOGICAL SETTING

Turkey is centrally located in the Mediterranean sector of the Alpine orogenic belt so it has many geothermal fields. This belt lies between the Russian belt to the north and the African and Arabian belts to the south (Günay and Şimşek, 1997). The geological history of the region was influenced by the repeated opening and closing of several oceans, traces of which are depicted as structure belts. An extensional tectonic regime prevailed in the Neogene, forming a series of grabens which related directly to geothermal activity in western Turkey. The Çeşme geothermal field is one of these. The Çeşme area is dominated structurally by faults having a general

north–south trend and discharging of thermal springs is directly associated with N–S and NE–SW-trending faults. The MTA (General Directorate of Mineral Research and Exploration of Turkey) drilled two deep wells, T24 and FY1, in 1974 and 1995, respectively, to obtain thermal water and to investigate the Çeşme geothermal area. Well FY1, which is 365 m deep (Yılmaz and Yakabağı, 1995) and passes through Neogene rocks from the surface (elevation is 10 m) to 316 m. Miocene tuffs and agglomerate occur between 0 and 100 m and Neogene sediments were cut between 100 and 316 m. At 316 m, Triassic limestones, which are the reservoir rocks of the Çeşme geothermal area, were drilled to well bottom. This well showed that the Neogene rocks are >300 m thick in some parts of the study area. Neogene rocks have low permeability and supposedly cap the geothermal system. Although they are relatively impermeable, fractured sandstone, marl and volcanic rocks form a second aquifer for thermal waters.

The Alaçatı area is 7 km south of Çeşme, west of İzmir (Figure 1). The lithological units exposed at Alaçatı (Çeşme) and nearby consist of sedimentary and volcanic rocks of Triassic to Quaternary age. Megalodont-bearing karstic limestones were dated as Middle–Upper Triassic by the investigations carried out

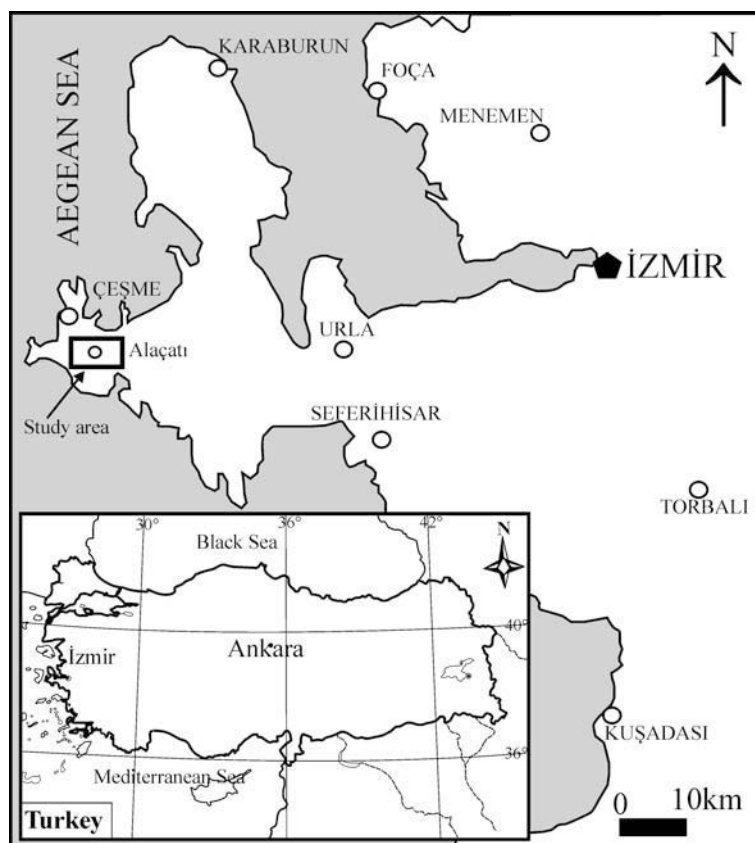


Figure 1. Location map of the study area.

around Karaburun and its surroundings by Erdogan *et al.* (1990). This karstic limestone is highly fractured. Lacustrine and volcanic sediments of Neogene age are located unconformably over karstic limestones. Lacustrine sediments are the combinations of limestone, marl, sandstone and claystone intercalations and the contact between lacustrine sediments and volcanic rocks are gradual. Agglomerates and tuffs are the volcanic rocks in the area, the Miocene tuffs of rhyolitic-dacitic composition being the most widespread pyroclastic rocks in the Alaçatı area. Although fractures are widespread in tuffs, they are difficult to identify due to the softness of the tuffs. Alluvium and slope wash are located over all rocks in the study area.

ANALYTICAL METHODS

About 40 grab samples were taken from the outcrops of the Alaçatı tuffs which cover an area of ~30 km². The map showing the locations of these sample and of the water samples described by Gemici (1999) and Gemici and Filiz (2001), are shown in Figure 2. Zeolites and coexisting minerals were identified by X-ray diffraction (XRD) analysis using a JEOL JSDX 100 S4 diffractometer. For the XRD analysis, pulverized powders were scanned from 4 to 60°2θ at a speed of 2°/min using Ni-filtered CuKα radiation. All powder samples were prepared using an automatic agate mortar. The clay mineralogy was identified from air-dried samples.

A JEOL SXA 733 scanning electron microscope (SEM) was used to examine the crystal habit, size and spatial relationships of the zeolites and other minerals. Chips ~10 mm in size were cemented on to 20 mm-diameter brass stubs and then coated with gold.

A JEOL 6060 SEM equipped with an energy-dispersive spectrometer (EDS) was used to obtain complementary semi-quantitative chemical data and images of the some authigenic minerals. Chips ~10 mm in size were cemented on to 32 mm-diameter aluminum stubs and then coated with gold-palladium.

CHEMICAL PROPERTIES OF WATER SAMPLES

The chemical composition of some selected thermal and cold groundwaters near Alaçatı, as reported by Gemici (1999) and by Gemici and Filiz (2001), are listed in Table 1. There are two types of thermal waters in the Çeşme geothermal field. The first is the NaCl type (e.g. the Ilıca and Şifne areas in Figure 2) which have temperatures of 42–58°C on the surface. These hot springs show high concentrations of Na which is a prominent component of seawater and they originated from a lower aquifer within the Triassic karstic limestone which is the main potential reservoir of the system. The second type is rich in Na and Ca but it has smaller Na contents and temperatures than the first type due to mixing with local groundwaters. These thermal waters

derived from an upper aquifer formed by Neogene lacustrine and volcanic sediments. Mixing of these thermal waters with the local groundwaters in different proportions gives rise to Na-Ca-Cl-HCO₃ thermal waters. According to Gemici (1999), the tuff outcrops in Alaçatı and in the area surrounding it are poor in groundwater (W10 in Figure 2).

RESULTS

Authigenic mineralogy

The silicic tuffs from the Alaçatı area are vitric but contain different amounts of crystals and lithic fragments. The vitric matrix of some of the silicic tuffs has generally been replaced by one or more authigenic minerals, such as mordenite, clinoptilolite-heulandite, smectite, calcite and opal-CT. The relative abundance of components for each sample in the study area was given by Kaçmaz and Köktürk (2004).

Mordenite

Mordenite is most abundant zeolite in the Alaçatı tuffs. It is present as needle-shaped fibrous or filiform crystals. The fibers are extremely delicate, from 0.28 to 0.86 μm in diameter. The different morphological types of mordenite include 'filiform', 'interlaced masses' and 'rat's-nest' features. In Figure 3, the mordenite is highly crystalline which suggests that all of the glass has been consumed. Some glass in the tuffs are replaced by zeolite minerals (Figure 4a), which consist of the silica-rich zeolite, mordenite. Figure 4a,b consists of two SEM images showing the dissolution texture of a glass and mordenite that has grown on the outside of the glass. Note the absence of textures that suggest that mordenite directly replaced the glass. Similar mordenite formation has been reported to occur in zeolitic tuffs of Kimolos Island, Greece (Fragoulis *et al.*, 1997). K-rich mordenite is an unusual mineral because its dominant

Table 1. Chemical composition of selected thermal and cold groundwater (mg/L) from the Çeşme geothermal area (Gemici, 1999; Gemici and Filiz, 2001).

	Ilıca*	Şifne*	W10 [†]
T(°C)	58	42	—
pH	6.5	6.65	7.58
Ec (μmho/cm)	26,600	48,400	2200
Ca ²⁺	677	1039	112
Mg ²⁺	367	762	29
Na ⁺	7108	9150	99
K ⁺	631	804	7
HCO ₃ ⁻	195	183	330
Cl ⁻	11,530	16,450	350
SO ₄ ²⁻	1665	2422	91
Water type	Na-Cl	Na-Cl	Ca-Na-Cl-HCO ₃

* hot spring

† cold groundwater

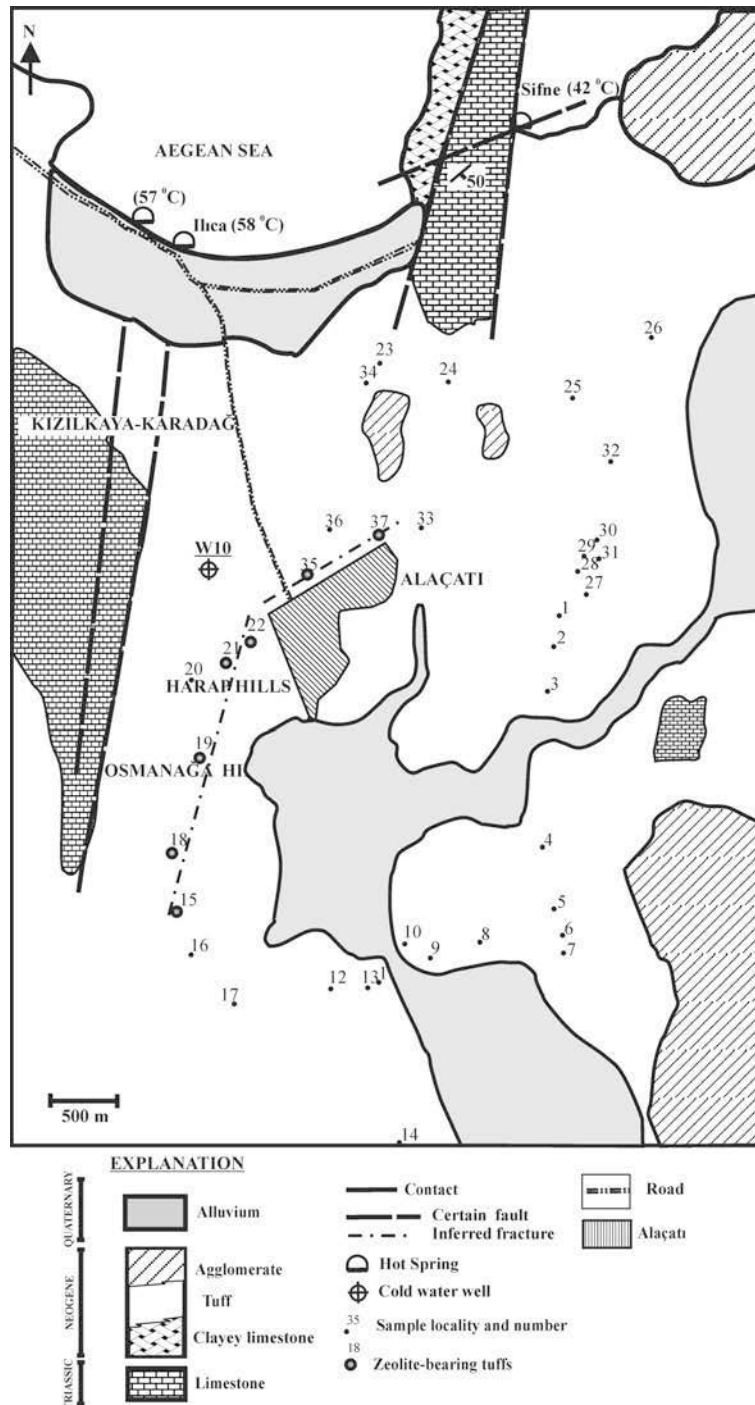


Figure 2. Geological map of the Alaçatı (Çeşme-İzmir) area, showing the sample locations and also water sample locations (spring and groundwater).

exchangeable cations are Na and Ca (Gottardi and Galli, 1985). We noted that the majority of the Alaçatı tuffs are dominated by Na- and Ca-mordenites. Semi-quantitative spectra obtained from selected crystals of mordenite minerals clearly indicate the strong presence of Na and Ca. The EDX analysis yields the major elements Si, Al, Na and Ca.

Mordenite was observed to coexist with clinoptilolite-heulandite, smectite and calcite, but its coexistence with clinoptilolite-heulandite is by far the most common association in the Alaçatı tuffs. Examination by SEM of some samples shows needle-shaped mordenite draped over clinoptilolite-heulandite, indicating that mordenite crystallized later than clinoptilolite-heulandite

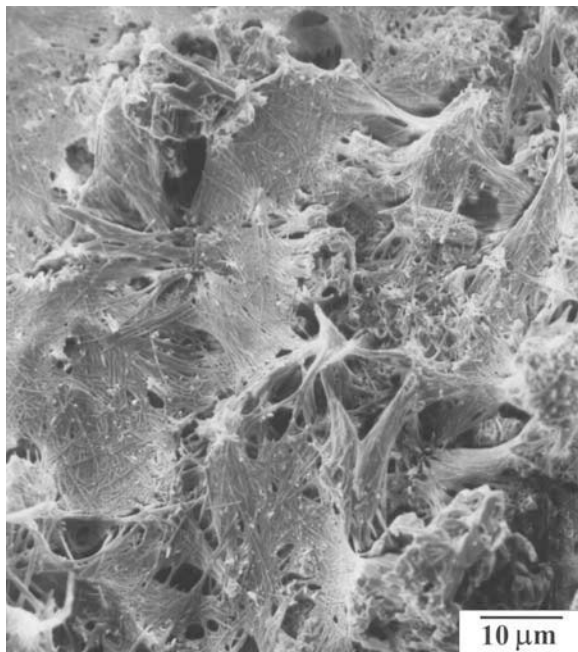


Figure 3. SEM image showing the total alteration of glass.

(Figure 5). Some clinoptilolite-heulandite minerals showed corrosion effects, presumably being the precursor for mordenite formation (Figure 6) (see discussion). The SEM examination of some samples shows that opal-CT lepispheres coexist with needle-shaped mordenite (Figure 7).

Clinoptilolite-heulandite

Mordenite, a high-silica zeolite mineral, is usually found with the heulandite minerals as an alteration product within volcanoclastic sequences (Kitsopoulos, 1997). Clinoptilolite-heulandite was found only in mordenite-bearing samples in the Alaçatı tuffs. Heulandite is similar in morphology to clinoptilolite,

but typically contains less K (Welton, 1984). Therefore, based on EDX spectra, we suggest that these authigenic zeolite minerals were, in general, heulandite minerals. The main ions in the heulandites are Na and Ca. In contrast, K was found to be present in minimal amounts.

Clinoptilolite-heulandite was observed to coexist with minerals other than mordenite and smectite in the Alaçatı tuffs (Figure 8). The coffin-shaped clinoptilolite-heulandite draped over smectite, (Figure 8) clearly indicates that the clinoptilolite-heulandite crystallized later than smectite. The needle-shaped fibers coating the clinoptilolite-heulandite are of mordenite. It can also be seen that the needle-shaped mordenite crystallized later than the clinoptilolite-heulandite as shown in Figures 5 and 6. In addition, it seems that the formation of clinoptilolite-heulandite followed that of smectite in Figure 9.

Smectite

Smectite is a widespread authigenic mineral in the Alaçatı tuffs and it has a characteristic honeycomb structure. The webby morphology, a common crystal habit of smectite, is seen in Figure 10. Identification of the smectite is based on XRD analysis supported by the EDX spectra showing the major elements of smectite (Si, Al, Fe, Mg and Ca with additional minor amounts of Na and K). It was determined as the only clay mineral. The abundant occurrence of smectite was found in zeolite-bearing tuffs (A15, A18, A19, A21, A22, A35 and A37). In addition, Samples A23 and A34 have abundant smectite despite being zeolite-free tuffs (see discussion). Smectite was apparently the first mineral to form (Figure 11). It rarely coexists with authigenic opal-CT (Figure 12) and where it coexists with other authigenic minerals, it is the earliest mineral to have crystallized (see Figures 8, 9, 11 and 12).

Opal-CT

The lack of diagnostic peaks of opal in XRD patterns indicates that opal, if present, is not abundant in the

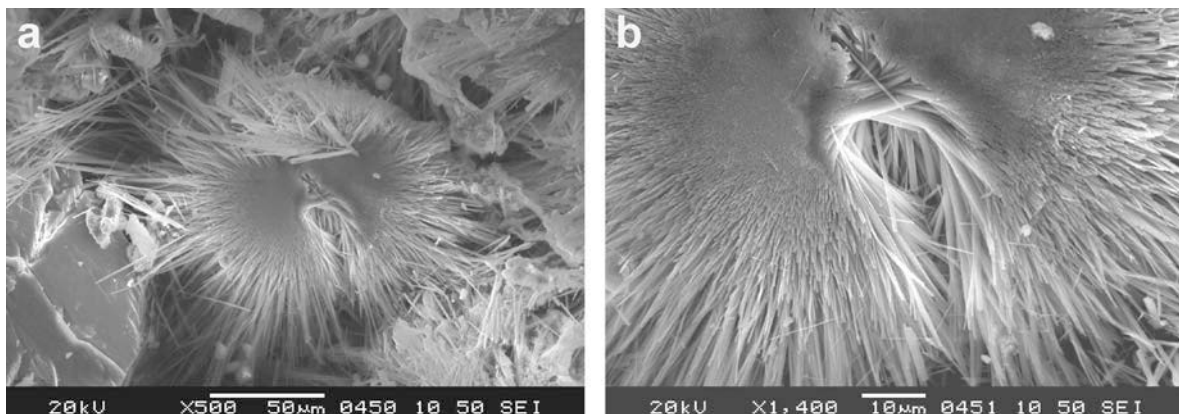


Figure 4. (a) SEM image showing the dissolution texture of a glass and needle-shaped mordenite that has grown on the outside of the glass. (b) Close-up view of part of Figure 4a. The center of the image is occupied by a glass shard showing replacement of mordenite.

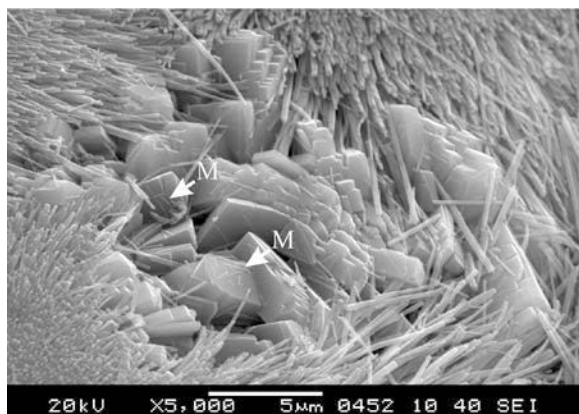


Figure 5. SEM image showing needle-shaped mordenite draped on clinoptilolite-heulandite, indicating that mordenite (M) crystallized later than clinoptilolite-heulandite.

Alaçatı tuffs. The bladed morphology of the lepispheres combined with the EDX spectra yielding only silica was used to identify this mineral as opal-CT. In some samples, the opal-CT lepispheres are associated with early-formed mordenite and smectite (see Figures 7, 12). The presence of opal-CT can be explained by excess non-reacted silica.

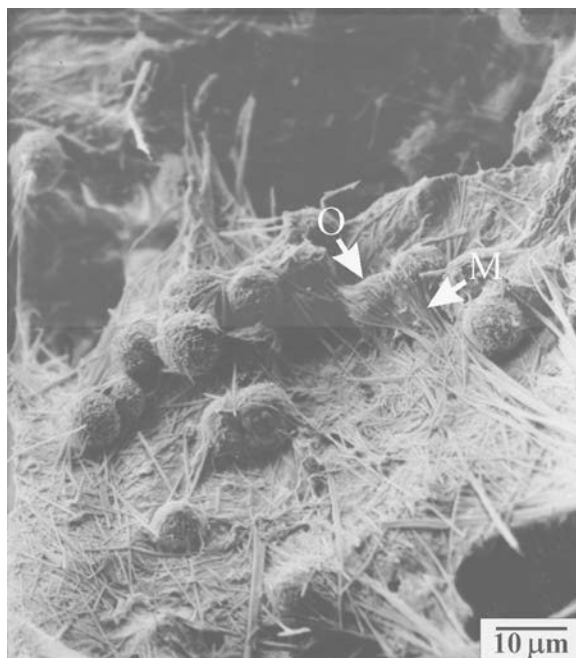


Figure 7. SEM image of opal-CT lepispheres (O) with mordenite (M).

Calcite

Calcite was observed in most of the samples. It locally replaced pyrogenic, epiclastic and authigenic minerals in the tuffs and was the last mineral to crystallize (Figure 13a); a close-up view of the calcite morphology is shown in Figure 13b. The EDX analysis consists primarily of Ca, the minor amounts of Si, Al and K probably being due to thermal waters. Calcite is draped over mordenite crystals (Figure 13a) clearly showing that the calcite crystallized later than mordenite.

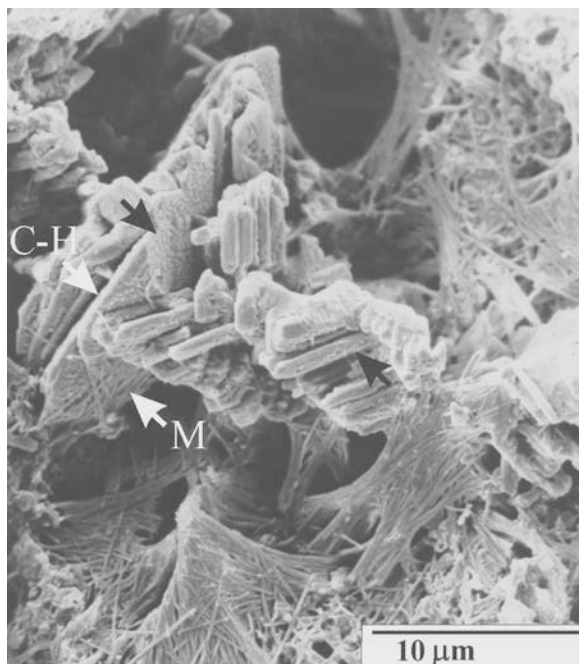


Figure 6. SEM image showing mordenite that grew on corroded clinoptilolite-heulandite. The clinoptilolite-heulandite was corroded prior to crystallization of fibers of mordenite that coat the clinoptilolite-heulandite. Clinoptilolite-heulandite can be seen, in the area shown by the black arrows, starting to corrode. M = mordenite, C-H = clinoptilolite-heulandite.

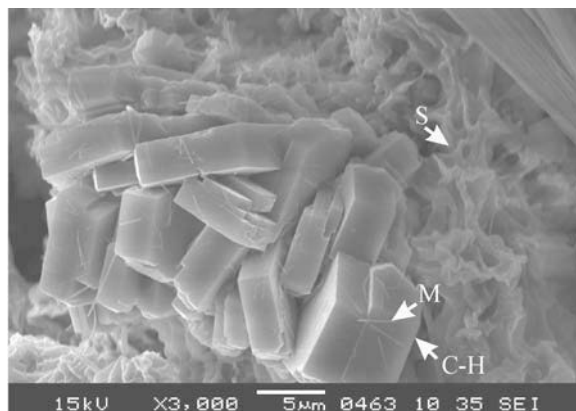


Figure 8. SEM image of sample A15 showing needle-shaped mordenite (M) and clinoptilolite-heulandite (C-H) with smectite (S). Thus, the paragenesis of zeolites, from early to late, is smectite, clinoptilolite-heulandite, and then mordenite.

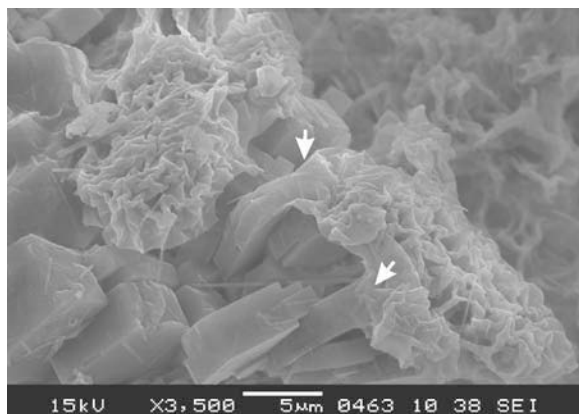


Figure 9. SEM image showing the formation of clinoptilolite-heulandite following that of smectite.

DISCUSSION

Formation of authigenic minerals

The mineralogical properties of the tuffs collected were investigated to discover how they were formed and to establish the relative age relationships of the zeolites and coexisting minerals. The tuffs in the Alaçatı (Çeşme) area have mainly been altered to mordenite and smectite. Clinoptilolite-heulandite, opal-CT and calcite complete the mineralogical suite.

Many previous works indicated that smectite is one of the main products of volcanic glass alteration in nature as well as in experimental studies (e.g. Caballero *et al.*, 1991; Tomita *et al.*, 1993). The formation of smectite

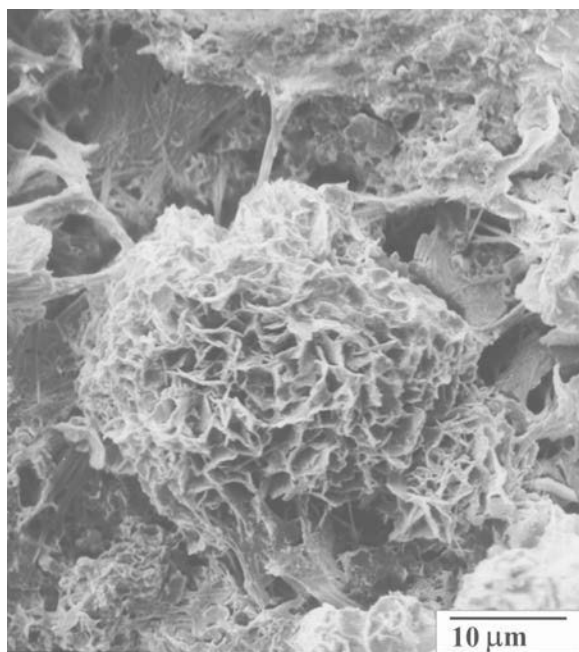


Figure 10. SEM image of pure smectite.

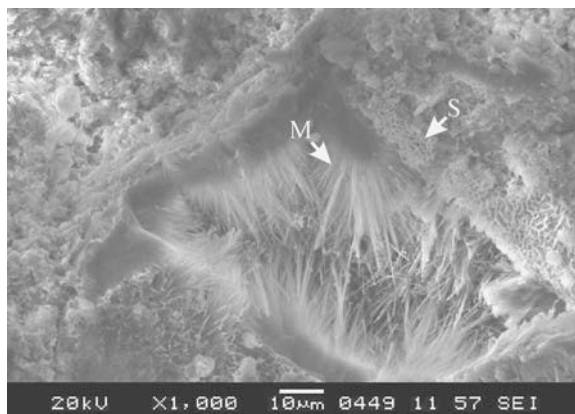


Figure 11. SEM image showing the glass shard consisting of needle-shaped mordenite (M) that grew on marginal smectite (S). Note that the outer walls of the glass shard are lined with a thin layer of smectite.

from an acidic protolith requires the removal of some excess Si and alkalis present in the protolith. A semi-open system facilitates this and results in the formation of extensive smectite deposits. If the system is fully open, all Si and alkalis are removed and smectite is the only phase present (Kitsopoulos, 1997). Smectite is present in trace to abundant amounts in most of the samples examined, but where prevalent, the smectite is related to the inferred fracture zone throughout the study area. It is as abundant as the zeolites along this fracture zone. The increase in smectite content may be attributed to the existence of a semi-open system in the Alaçatı area. However, the presence of zeolites and opal-CT in these tuffs indicates that sufficient Si and alkalis were retained to form these minerals. Hence, a semi-open system that changed into smaller closed systems is postulated. Meanwhile, large amounts of smectite were determined in other samples (A23 and A34) away from the fracture zone. The lack of zeolites and the presence of abundant smectite in these samples appear to be



Figure 12. SEM image of opal-CT lepispheres (O) with smectite (S).

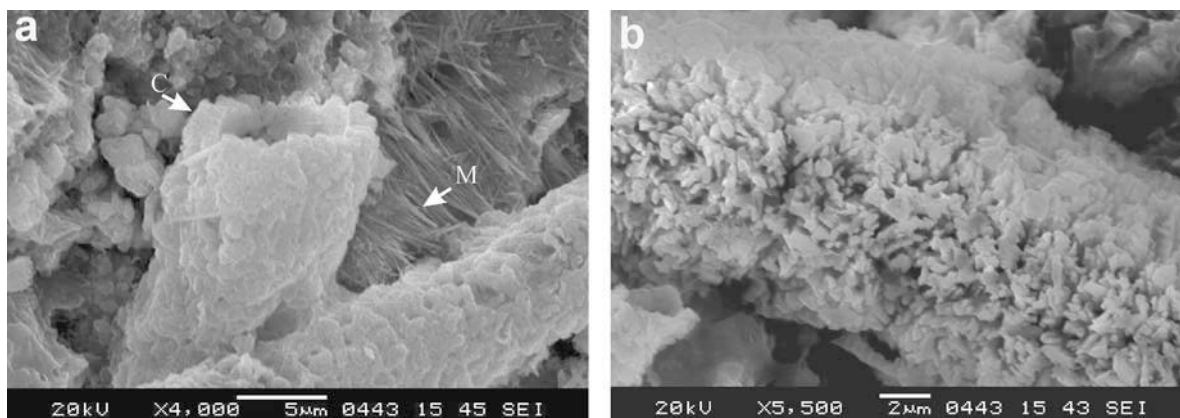


Figure 13. (a) SEM image of calcite (C) with mordenite (M); (b) close-up view of the calcite morphology.

related to extension of the fault into tuffs in the northern part of the study area.

Smectite was apparently the first mineral to form; the outer walls of some of the glass shards are lined with a thin layer of smectite (Figure 11). Note that the inner part of the glass shard is replaced by acicular mordenite. Examination by SEM of some samples shows that opal-CT coexists with early-formed smectite (Figure 12). Opal-CT peaks were not detected by XRD, although its crystalline habit and the EDX spectrum suggest that this mineral is opal-CT. At this stage, the excess silica was probably present in the solution and opal-CT formed later than smectite.

The pH of the fluids might have ranged between 7 and 9 in order for the siliceous zeolite, clinoptilolite, to form (Sheppard *et al.*, 1988). Subsequent alteration of glass to smectite would have raised the pH, a_{SiO_2} and the $(\text{Na}+\text{K})/\text{H}^+$ activity ratio, providing a chemical environment favorable for the formation of the heulandite-type zeolites, depending on the initial composition (Hay, 1966; Hay and Sheppard, 1977; Hay and Guldman, 1987). Clinoptilolite-heulandite was the first zeolite to form in the Alaçatı tuffs. Direct connection is observed between clinoptilolite-heulandite and smectite. The white arrows in Figure 9 indicate that the formation of smectite ceased and clinoptilolite-heulandite continued to form from remaining liquid. The pseudomorphic replacement of glass shards by clinoptilolite, commonly described by Leggo *et al.* (2001) and Cochemé *et al.* (2003), was not seen in the tuffs studied here. The EDX analysis was used to identify these crystals as generally heulandite. The EDX spectra generally contain the elements typical of heulandite: Si, Al, Ca and Na; K was found in minimal amounts. Likewise, zeolite-bearing tuffs contain between 2.63 and 3.06 wt.% K_2O , whereas zeolite-free tuffs contain between 2.68 and 4.28 wt.% K_2O (more detail given by Kaçmaz and Köktürk, 2004). The stages of alteration leading to the formation of zeolite-bearing tuffs also show a decrease in K_2O .

Mordenite was the last zeolite to form in the Alaçatı tuff and it is commonly draped over clinoptilolite-heulandite, although some mordenites develop from the volcanic glass. Likewise, as shown in Figure 4a,b, the glass has been leached and mordenite formed *in situ* from volcanic glass, as commonly described (*e.g.* Ghiara *et al.*, 1999; Christidis, 2001; Brathwaite, 2003) in vitric tuffs. Some opal-CT lepispheres appear with mordenite. During the alteration, the crystallization of mordenites resulted in an excess of SiO_2 that crystallized chiefly as opal-CT. As shown in Figure 7, the needle-shaped mordenites are draped over opal-CT lepispheres. It seems as if the opal-CT lepispheres formed earlier than the needle-shaped mordenite. In fact, opal-CT formed last. Opal-CT lepispheres probably penetrated the earlier-formed mordenite needles at this stage.

The hydrothermal experiments (Kusakabe *et al.*, 1981) showed that mordenite was formed from clinoptilolite at greater pH and Na concentrations. However, it is known that Na is usually found in greater amounts within the mordenite structure than within that of heulandite (Bowers and Burns, 1990). There was substantial evidence to support a hypothesis that mordenite was formed later than clinoptilolite-heulandite minerals in the Alaçatı tuffs. Its coexistence with clinoptilolite-heulandite is the most common association in the Alaçatı tuffs and where mordenite and clinoptilolite-heulandite coexist, the mordenite is always draped over clinoptilolite-heulandite (Figures 5, 6, 8). Increase in the pH and cation ratios of the remaining liquid were probably responsible for the formation of the mordenite that crystallized after clinoptilolite-heulandite. Meanwhile, a pitted morphology of the trace amounts of clinoptilolite-heulandite crystals was observed using SEM (black arrows in Figure 6). During alteration of the Alaçatı tuffs, local slight changes in the pH and cation ratios of the thermal water were probably responsible for the pitted morphology. However, it is important to note that intact clinoptilolite-heulandite crystals were also commonly found within samples. The degree of the

corrosion of the clinoptilolite-heulandite crystals was probably dependent on the pH and Na concentrations of the thermal waters.

Mordenite and clinoptilolite occur in both fresh and saline water environments. Their coexistence, coupled with the absence of phillipsite, also characterizes low-temperature hydrothermal alteration (Iijima, 1974). Experimental work by Hawkins *et al.* (1978) in hydrothermal areas suggests that clinoptilolite and mordenite should dominate the low-temperature (<150°C) mineral assemblages. Phillipsite should be absent from these regions because it is unstable with respect to clinoptilolite and mordenite. Furthermore, solution composition has an increasingly important control on the reaction products. Phillipsite apparently requires strongly alkaline solutions for its formation. Mordenite may form in Na-rich solutions, phillipsite may form preferentially in K-rich solutions, and the greater Al:Si ratio favors the formation of phillipsite. The absence of phillipsite and the formation of mordenite and clinoptilolite-heulandite were due to the associated presence of Na- and Ca-rich thermal waters and silica-rich glass which provided the high Si:Al ratio in the Alaçatı tuffs. K-mordenite, formed by the hydrothermal alteration of tuffs (Pe-Piper and Tsolis-Katagas 1991), is not present in the Alaçatı tuffs and this is in accordance with Na and Ca-rich thermal waters and mobilization of K during the alteration process.

An experimental study by Fuente *et al.* (2002) of the hydrothermal alteration of volcanic glass indicates that Na-rich solutions promote smectite formation with increasing time, and K-rich solutions promote the formation of illite. In the latter case, the temperature should also be high enough. Kalogeropoulos and Mitropoulos (1983) indicated that a temperature of 140–170°C is adequate to initiate the illitization of smectite. Kitsopoulos (1997) stated that the smectites are affected by illitization under increasing temperature conditions at Polyegos. Smectite is the only clay mineral in the Alaçatı tuffs. The absence of illite indicates that whether the problem is temperature or chemical composition, the thermal waters in the present study are not suitable for the illitization of smectite. However, detailed studies by Ma *et al.* (1995) of the alteration mineralogy of lacustrine tuffs and siltstones in the upper part of the Wairakei system, indicate that mordenite and associated smectite were formed at temperatures of <110°C. Experimental work by Gemici and Filiz (2001) indicates that the reservoir temperature of the Çeşme geothermal area is estimated to be 85–100°C.

The formation of Na- and Ca-rich minerals, such as mordenite and clinoptilolite-heulandite, should have left the thermal waters Ca-rich. The enrichment of Ca is attributed also to the increased Ca content of thermal waters which circulate through the Triassic limestone that are present at depth as reservoir rocks. The presence of authigenic calcite is consistent with enrichment of Ca

during the alteration process. Any excess Ca would form calcite. The EDX spectrum of calcite reveals Ca as the major element with minor amounts of Si, Al and K also present. The presence of K within calcite is also consistent with mobilization of K during the alteration process. The mobile behavior of K in the zeolite-bearing tuffs is further evidence for interaction of K in the thermal water and the tuffs. Calcite is probably the latest phase because most of the coexisting mineral surface is covered by calcite. However, calcite is commonly found to drape over mordenite (Figure 13a,b), clearly showing that the calcite crystallized later than mordenite.

CONCLUSIONS

The relationships between zeolites and coexisting authigenic minerals were determined by using SEM, and a possible mechanism of formation of the authigenic minerals is suggested. The co-existence of zeolites with smectite suggests that the Alaçatı zeolites formed in a semi-open system which subdivided into smaller closed systems. Smectite was apparently the first mineral to form and locally it is found to coat the vitric material. Opal-CT occasionally coexists with smectite and the needle-shaped mordenite. It was formed after the smectite and mordenite. The minor amount of opal-CT probably reflects the minor amount of silica that was left over after the smectite and mordenite formed from the glass, which, being of rhyodacite-dacite composition, had an intermediate silica content (>60% SiO₂). Clinoptilolite-heulandite probably crystallized before mordenite in the Alaçatı tuffs. Where mordenite and clinoptilolite-heulandite coexist, the mordenite is always draped over clinoptilolite-heulandite. Examination by SEM proved that mordenite was the last zeolite mineral to form in the tuffs. Likewise, some mordenite crystals grew on clinoptilolite-heulandite and these zeolites had been corroded prior to the crystallization of the mordenite. The mineral corrosion was due to the chemistry of thermal waters. Thus, from early to late, the sequence is: mordenite and calcite. The formation of mordenite should have left the thermal water Ca-rich. An increase in Ca might have favored the formation of calcite.

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