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Geological, mineralogical and geochemical characteristics of zeolite deposits associated with borates in the Bigadiç, Emet and Kirka Neogene lacustrine basins, western Turkey

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Abstract. The Bigadiç, Emet and Kirka lacustrine basins of western Turkey may be considered as Tibet-type graben structures that were developed during the Miocene within the Izmir-Ankara suture zone complex. The volcanic-sedimentary successions of these basins are made up of mudstone, carbonate (limestone and dolomite) and detrital rocks, and also of crystal or vitric tuffs about 135 to 200 m thick. The Degirmenli (Bigadiç), Emirler (Bigadiç) Köpenez (Emet) and Karaören (Kirka) tuffs constituting the zeolite deposits are situated beneath four borate deposits (colemanite, ulexite, borax). The most abundant diagenetic silicate minerals are K- and Ca-clinoptilolites in the zeolite deposits, and Li-rich trioctahedral smectites (stevensite, saponite and hectorite) and K-feldspar in the borate deposits. In the Degirmenli, Emirler, Köpenez and Karaören deposits, the following diagenetic facies were developed from rhyolitic glasses rich in K and poor in Na: (glass + smectite), (K-clinoptilolite + opal-CT), (Ca-clinoptilolite + K-feldspar ± analcime ± quartz) and (K-feldspar + analcime + quartz). K-feldspar which is also rarely associated with phillipsite (Karaören) and heulandite (Degirmenli and Karaören), succeeds clinoptilolite and precedes analcime in these diagenetic facies where dioctahedral smectites, opal-CT and quartz are the latest minerals. No diagenetic transformations exist between clinoptilolite, K-feldspar and analcime that were formed directly from glass. The lateral facies distributions resulted from the differences in salinity and pH of pore water trapped during deposition of the tuffs, but vertical distributions in vitric tuffs seem to have been controlled by the glass/liquid ratio of the reacting system and the permeability or diffusion rate of alkali elements. The Bigadiç, Emet and Kirka zeolite deposits which were formed in saline basins rich in Ca and Mg ions, show similar chemical changes, i.e. loss of alkalis and gain in alkaline-earth elements that have taken place during the diagenetic transformation of rhyolitic glasses to dioctahedral smectites or clinoptilolite. The absence of sodic zeolites such as mordenite, erionite, chabazite and silica-rich phillipsite is mainly due to the very high K/Na ratio of the starting materials rather than initial alkaline conditions or high Na content in lake waters.

During the Neogene to Quaternary, several lacustrine basins were developed in western Turkey (Fig. 1). The Neogene basins were filled up by clayey, carbonaceous and sandy sediments, and also by explosive products of contemporaneous K-rich calc-alkaline volcanism showing various degrees of crustal contamination (Yilmaz 1989, 1990; Güleç 1991). These basins are generally represented by a volcanic-sedimentary succession and contain, in some regions, very important resources of fossil fuel and industrial minerals, such as lignite, bituminous shale, clays, borates and zeolites.

The first mineralogical studies related to zeolite exploration in western Turkey showed that clinoptilolite and analcime were the commonest minerals in some of these basins, particularly borate-containing ones (Ataman 1977; Ataman and Gündogdu 1982). Later, the geological, mineralogical and geochemical characteristics of the Bigadiç, Emet and Kirka basins, which contain zeolite-borate associations, were investigated in detail mainly by the authors of this study (Gündogdu 1982; Gündogdu et al. 1989; Yalçin 1984, 1988; Semelin 1985; Temel 1987). These studies revealed that clinoptilolite was the major constituent of four very thick tuffs (Degirmenli and Emirler in Bigadiç, Kopenez in Emet, and Karaören in Kirka) which are the largest clinoptilolite deposits of known sedimentary zeolite formation in Europe (Gottardi and Obradovich 1978). For example, the outcropping part of the Emirler deposit of Bigadiç amounts about 1.4 billion metric tons (Baysal et al. 1986) and its average clinoptilolite content is 85%.

In this study, the distribution and formation of zeolites and associated diagenetic minerals in these deposits, is

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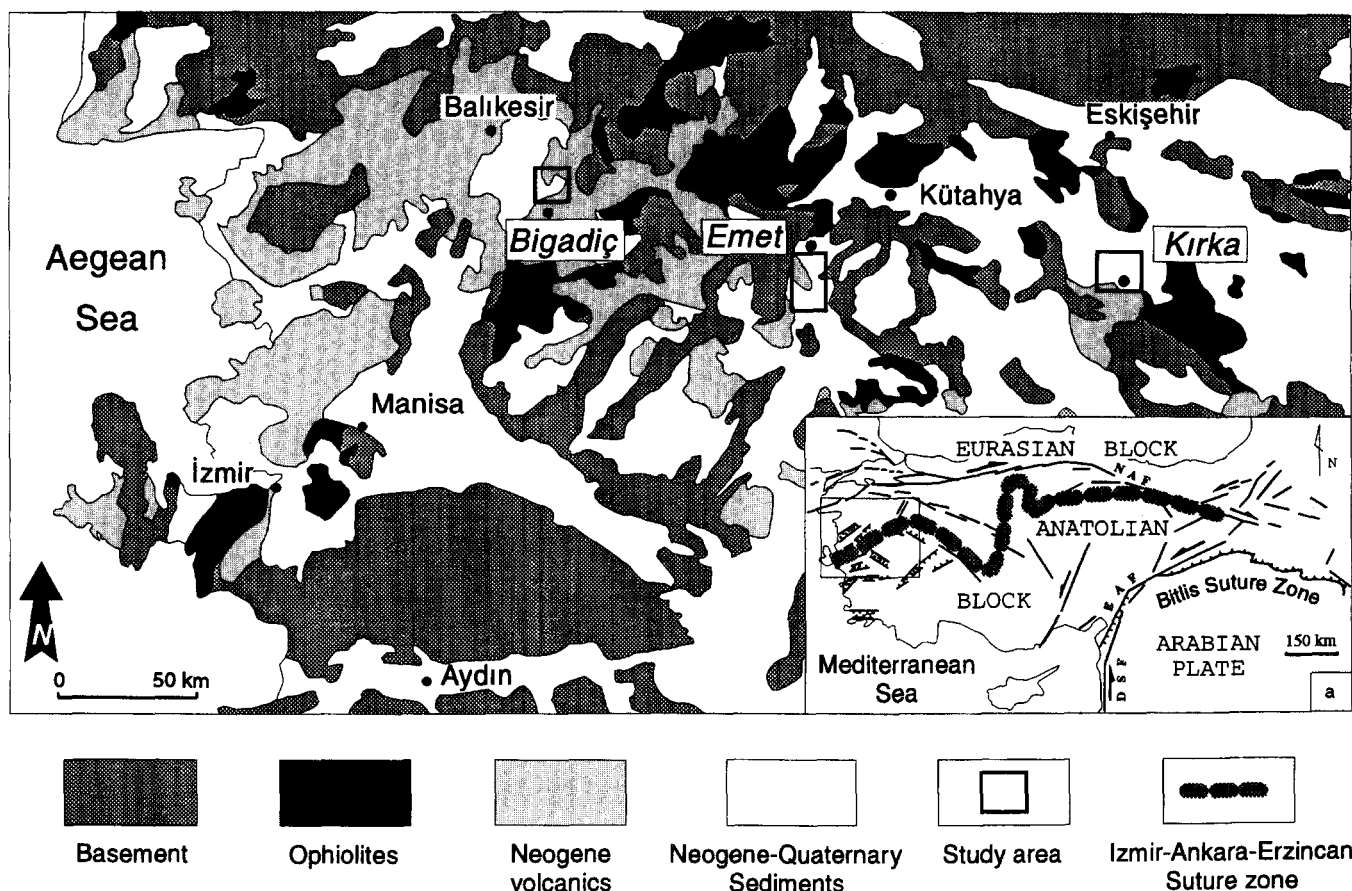
Fig. 1. Simplified geological map of western Turkey (prepared from Geological Map of Turkey, scale 1:2 000 000) and sketch **a** showing major tectonic structures of Turkey (*DSF*, Dead Sea Fault; *NAF*, North Anatolian Fault, *EAF* East Anatolian Fault)

reviewed on the basis of geological, mineralogical and geochemical data.

Tectonic setting

According to regional geodynamic models (Sengör and Yilmaz 1981; Sengör et al. 1985), the tectonic evolution of western Turkey since the early Miocene is controlled by two collisions developed along the Izmir-Ankara-Erzincan and Bitlis sutures (Fig. 1a). The N–S intracontinental convergence associated with the Paleocene-Eocene Izmir-Ankara-Erzincan suture continued until the late Miocene (Sengör and Yilmaz 1981). On the other hand, the middle Miocene Arabia-Eurasia collision, along the Bitlis suture in southeastern Turkey (Sengör and Yilmaz 1981), resulted the westward tectonic escape of the Anatolian block from the east Anatolian convergent zone to the Aegean subduction system, mainly along the North and East Anatolian strike-slip faults (e.g. McKenzie 1972; Sengör et al. 1985). This escape, accepted also as the beginning of the neotectonic period in Turkey (Sengör 1980), generated a N–S extensional regime in western Turkey since the late Miocene (Sengör et al. 1985). Recently, it has been proposed, in addition, that N–S extensional tectonics began in the latest Oligocene-early Miocene period (Seyitoglu and Scott 1991; Seyitoglu et al. 1992). However, the existence of several strike-slip faults cutting the units older than upper Miocene (Semelin 1985), and a general uplift at the south of Emet Basin before this time (Semelin 1985; Yalçin et al. 1985) rather support the hypothesis of Sengör et al. (1985).

During this tectonic evolution, a large number of northeast and northwest-trending basins such as Bigadiç, Emet and Kirka were

developed within the Izmir-Ankara suture zone which is occupied by ophiolitic, metamorphic and sedimentary rocks of Permian to Eocene age (Fig. 1). In the Bigadiç, Emet and Korka basins, the main tectonic structures affecting the Miocene units are the oblique faults and roll-over type folds that are generally parallel to the trends of the basins and the Izmir-Ankara suture (Figs. 2, 3 and 4). E–W trending normal faults, compatible with a late Miocene N–S extensional regime, are rarely observed (e.g. the Bigadiç basin). Therefore, these basins may be Tibet-type grabens that were formed during the last compressional phases of the paleotectonic evolution of western Turkey, as already supposed by Sengör et al. (1985). The similarity between the volcanism in western Turkey and Tibet, both being rich in K_2O (Yilmaz 1989, 1990; Arnaud et al. 1992) and developed on suture zones, may be considered as additional data supporting this structural interpretation.

Stratigraphy and lithology

Bigadiç basin

The northeast-trending Bigadiç basin is located to the southeast of Balikesir (Fig. 1). The volcanic-sedimentary succession rests on Upper Cretaceous meta-sandstones and meta-limestones of the Izmir-Ankara suture zone and the calc-alkaline andesitic lavas of lower Miocene age (basement rocks and basal volcanics, see Fig. 2). The andesites represent the first volcanic event in the region (22.3 Ma: Gündogdu et al. 1989) and cover a large area (see Figs. 1, 2). The lower to upper Miocene succession which is about 700 m thick (Gündogdu et al. 1989), is named the Bigadiç formation and is
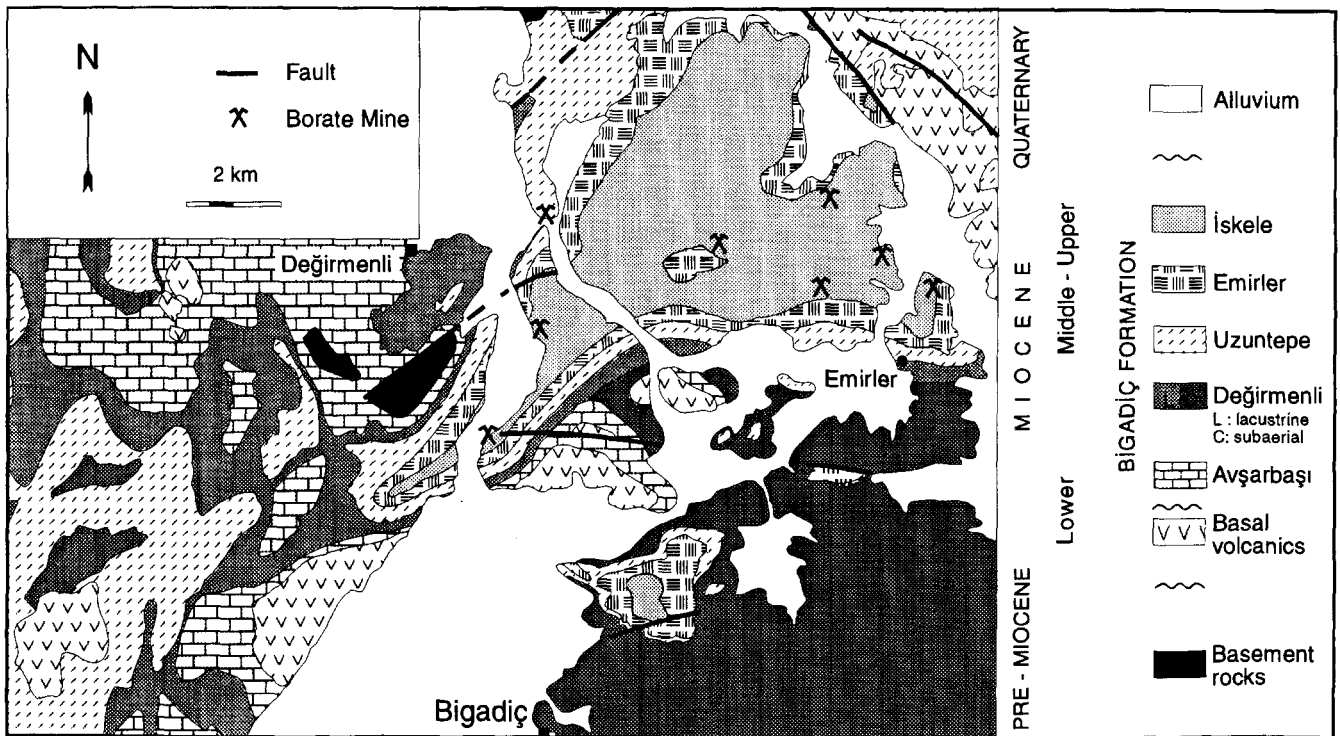
Fig. 2. Geological map of the Bigadiç basin (compiled from Gündogdu 1982; Baysal et al. 1986)
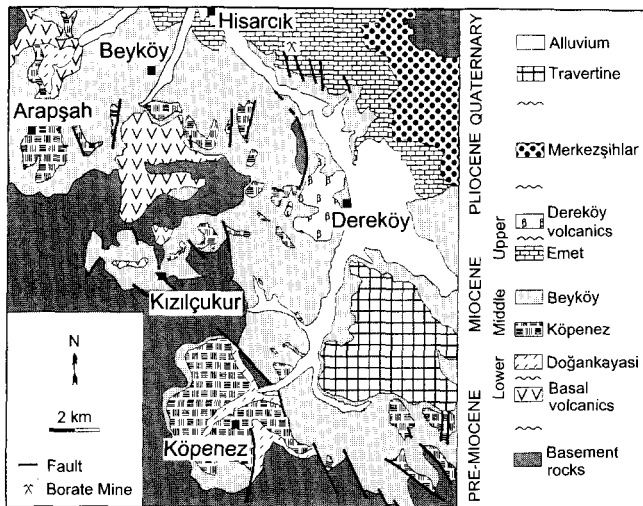

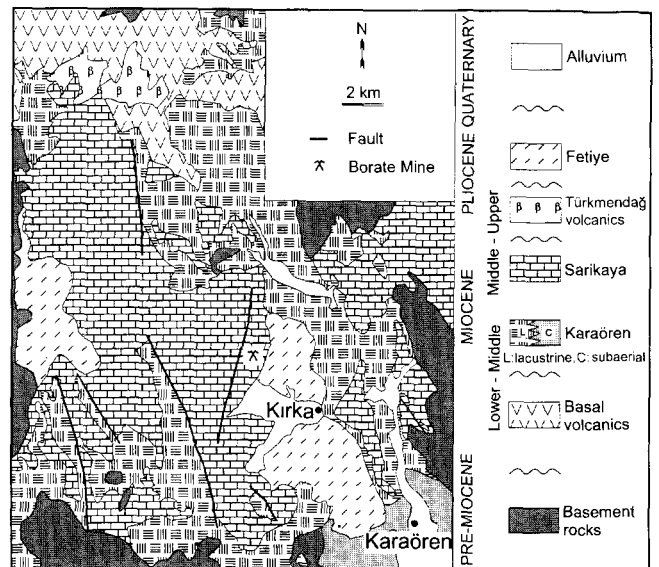**Fig. 3.** Geological map of the southern part of the Emet basin (from Yalçin et al. 1985)

Fig. 4. Geological map of the Kirka basin (from Yalçin 1989)

divided into the following members by Gündogdu (1984): Avşarbaşi, Degirmenli tuff, Uzuntepe, Emirler tuff and Iskele members (Fig. 2).

The Avşarbaşi member is the first sedimentary unit that indicates the formation of the Bigadiç paleolake in the early Miocene period. This unit, with an average thickness of 110 m, consists of carbonaceous, clayey and tuffaceous rocks and outcrops extensively in the west of the study area. It begins with dolomicrites intercalated with a few tuffs, and ends with laminated shales, marls and siliceous limestone containing mainly calcite and dioctahedral and trioctahedral smectite. A small amount of clinoptilolite is found in the tuffaceous rocks.

The Degirmenli tuff member, which represents the first major explosive volcanic event in the region, is composed of lacustrine and

subaerial tuffs of dacitic to rhyodacitic composition, with lateral transition into each other. The lower and middle parts (100 m) of the lacustrine facies, the first zeolite deposit in the Bigadiç basin, consist of dark grey and coarse-grained crystal tuffs, which contain biotite, feldspar (mostly andesine), quartz and hornblende as pyroclasts in order of abundance. These commonly unaltered components and a minor amount of pumice and volcanic rock fragments are bounded by mainly volcanic matrix of dust size and rarely by carbonate cement. The crystal tuffs have generally high crystal/matrix ratio (up to 70%), and are intercalated with light-grey and medium to fine-grained tuffs. The uppermost part of the unit (35 m) is formed only by very fine-grained tuffs, of which the constituents are not

recognizable even in thin-sections apart from sparse biotite. Zeolitization is only developed in pumices, in the matrix of coarse-grained crystal tuffs and in fine-grained tuffs. No other epiclastic or carbonaceous rock intercalations were observed within this unit which shows a general fining-up tendency. These characteristics, very similar to those of air-fall deposits, indicate that explosive volcanism of Plinian type was developed within a short period of time but with successive eruptions. An average K-Ar age of 17.6 Ma for biotites places this tuff in the uppermost part of the lower Miocene (Gündogdu et al. 1989).

The Uzuntepe member of the middle Miocene which forms the first borate deposit in the area, is about 115 m thick and starts with a borate zone of 30–40 m. This zone consists of an alternation of thin-bedded limestones, marls, shales and tuffs with intercalations of lens-like borate deposits. The middle and upper parts of the section are composed of siltstone/claystone intercalated with thick bedded cherty limestone and alternation of limestone-claystone-tuff, respectively. The varve-like structures formed by light (carbonate) and dark (clayey or very fine-grained tuff) coloured laminae, are the most common primary sedimentary structures in this units as well as in the Iskele member, which is the second borate unit (Gündogdu and Gökçen 1983; Temel and Gündogdu 1988). The clayey-carbonaceous rocks contain trioctahedral smectites rich in Li, calcite, dolomite, aragonite and rarely strontianite, whereas in the tuffs K-feldspar, clinoptilolite, analcime, quartz, biotite, smectite, scarce hornblende and opal-CT are found. The main borate minerals are colemanite, probertite and ulexite. Locally howlite and hydroboracite together with anhydrite, gypsum and celestite are also present (Gündogdu 1982; Temel 1987).

The next unit, the Emirler tuff member in the lacustrine facies, is a product of the second major explosive volcanic event in the area. This unit with an average thickness of 200 m, consists of rhyolitic vitric tuffs that were extensively transformed into zeolites. As is the case in the Degirmenli tuff member, the lower and middle parts of the unit (150–165 m) are generally formed of coarse-grained tuffs with medium to fine-grained tuff intercalations and the last part of 35–55 m is completely made up of very fine-grained tuffs. This may indicate that the emplacement mechanism described for the Degirmenli member is also valid for the Emirler tuffs. Coarse-grained tuffs with vitroclastic texture dominantly contain fibrous pumice and porous glass shards, whereas very fine-grained tuffs are similar to marl and their constituents are not visible in the field and in the thin-sections. The size of the pumice fragments, which are randomly distributed within volcanic material of dust particle size, reaches 5–15 cm in some horizons. The total amount of pyrogenic minerals (quartz, andesine and biotite) and lithoclasts (mainly volcanic) is about 5% and does not exceed 15% (Temel 1987). Zeolitized tuffs are light yellow to green, resistant and relatively hard, while unaltered ones are typically white to light grey, friable and soft. Original textures of dark-green pumice fragments are generally preserved in the zeolitized tuffs. On the other hand, the highest K-Ar age obtained from clinoptilolites in fine-grained tuffs (14.3 ± 2.1 Ma) would place this unit in the middle Miocene (Gündogdu et al. 1989).

The last unit, the Iskele member of the middle-upper Miocene, is about 150 m thick and consists of shales, marls, limestones and tuffs. The second borate deposit in the area was developed within the lower part of this member (50–60 m). Clayey-carbonate rocks are made up of Li-stevensite, Mg- and Al-Fe saponite, K-feldspar, calcite, dolomite and aragonite (Gündogdu 1985). Trace amounts of magnesite and strontianite were also observed in the central part of the basin (Temel 1987). Clinoptilolite and analcime associated with K-feldspar, are only found in some tuff levels. Economic borate minerals are colemanite and ulexite, and pandermite and tunellite locally encountered with anhydrite and celestite.

Emet basin

The Emet basin of northwest-trend is located within the boundaries of Kütahya province (see Fig. 1). Zeolitized pyroclastics and other lithostratigraphic units outcrop especially in the southern part of the basin (south of Hisarcik), whereas the northern part is commonly covered by the borate-bearing unit (Yalçin 1984; Semelin 1985; Yalçin et al. 1985). Therefore, the data presented here concern essentially the southern part where the Paleozoic metamorphic and Mesozoic carbonate rocks of the Izmir-Ankara suture, and the Neogene volcanics unconformably underlie the volcanic-sedimentary succession of the Emet basin (Fig. 3). Meteoric alterations and karstification were intensively developed within metamorphic (gneiss, schists, marbles) and carbonate rocks (recrystallized limestone, dolomite, dolomitic limestone) that surround the basin. K-rich rhyodacitic and rhyolitic volcanic rocks (Semelin 1985) commonly altered into kaolinites, are comparable to the products of the lower Miocene volcanic episode in the Kütahya region (Becker-Platen et al. 1977; Bingol 1977).

The lower-to-upper Miocene volcanic-sedimentary succession of about 800 cm thick is divided into four units: the Dogankayasi, Köpenez, Beyköy and Emet formations. They are cut by the upper Miocene Dereköy volcanics and unconformably overlain by the Pliocene Merkezşihlar formation (Yalçin 1984; Semelin 1985; Yalçin et al. 1985).

The Doğankayasi formation of lower-middle Miocene age is about 85 m thick and consists of an alternation of organic-rich laminated limestones, sandstones and marls in the southern part of the basin. Some vitric tuff beds, intercalated with laminated limestones, are observed within the lower part of the unit and they contain K-feldspar, analcime and quartz. These are a sign of the initiation of explosive volcanism which becomes intensive during the deposition of the next unit.

The Köpenez formation of middle Miocene age, containing zeolite deposits in the study area, consists dominantly of vitric tuffs that are light-grey to dark-green in colour. Coarse- to very coarse-grained tuffs interbedded with medium- to fine-grained tuffs are the predominant lithologies in the lower and middle parts of this unit of about 200 m thickness, the upper part being represented only by very fine-grained tuffs (Yalçin et al. 1985) as in the Emirler tuff member of the Bigadiç Basin. Colours and petrographic characteristics of these tuffs are also similar to those of the Emirler tuffs. However, the Köpenez coarse-grained tuffs contain more angular pyrogenic crystals (mostly andesine and biotite) and lithoclasts of volcanic and metamorphic origin (Yalçin 1984; Semelin 1985). The quantity and grain size of clasts in the ash tuffs increases from the northwest toward the southeast, which suggests a source area in the south (Semelin 1985; Yalçin et al. 1985). In addition, the Köpenez tuffs are intercalated with several laminated limestone horizons 1 to 15 m thick. They form about 20% of the stratigraphic section of the unit and correspond to relaxation periods between Plinian eruptions. At some levels of the coarse-grained tuffs, laminated limestones are observed as discs and balls of 1 to 50 cm in diameter, indicating an intrabasinal reworking process due to tectonic instabilities (Semelin 1985). These carbonate rocks, mainly containing calcite and a small amount of dolomite, opal-CT or quartz and organic matter, are similar to those observed in the Doğankayasi formation and at the base of the Beyköy formation (Yalçin 1984; Semelin 1985; Yalçin and Gündogdu 1987). According to Semelin (1985), laminated limestones that are represented by couplets of (calcite-diatomite)-organic matter or calcite-organic matter, suggest a stratified or meromictic lacustrine environment, particularly in the southern part of the basin. They are also common in saline-paleolake deposits (Hardie et al. 1978), as well as in the trona deposit of the Beypazari basin (central Anatolia), where the trona is associated mainly with K-feldspar, saponite and sepiolite and less commonly with analcime and searlesite (Gündogdu et al. 1985). This basin was developed contemporaneously with the Kizilcahamam volcanism of Miocene age, which is relatively rich in Na compared to volcanism in western Turkey (Gündogdu et al. 1994).

The middle Miocene Beyköy formation, which is 200 m to 350 m thick, is made up of laminated carbonate rocks within the first 60 m. The upper part is represented only by epiclastic rocks that were deposited in alluvial cone, fluvial and lacustrine environments from the north toward the south (Yalçin 1984; Yalçin et al. 1985; Semelin 1985). In the northwest of the study area, red-coloured alluvial rocks

show an alternation of poorly sorted and consolidated sandstones, conglomerates and sandy marls. The fluviatile facies of the central part is formed especially of arkosic sandstones and includes coal beds at some levels. Fine-grained and thinly bedded distal turbiditic sandstones which contain primary sedimentary structures such as flute, groove and prod casts, are observed in the lacustrine parts to the southeast. The distribution of facies as well as the primary sedimentary structures, indicates that the main direction of sediment transport was NW to SE. Following the deposition of these clastics which correspond to an active N–S compressional tectonic period in the region (Semelin 1985), the paleolake dried-up completely in the south and migrated to the north as a result of a general uplift of the southern part of the basin (Yalçin et al. 1985; Semelin 1985). This is also supported by the distribution of the borate-bearing Emet formation which covers a large area to the north of Hisarcik, as already mentioned (see Fig. 3).

The Emet formation of upper Miocene age has a thickness of 120–250 m and contains cherty limestone and dolomite at the bottom and claystone/marl at the top, with borate lenses as two zones in the lower-middle part. The lower borate zone is 75 m thick, while the upper borate zone is 25–35 m thick. Borate deposits are mainly formed of nodular colemanite and ulexite of economic importance; locally hydroboracite and probertite are found. The other authigenic minerals such as sulphate (gypsum, celestite), elemental sulphur, realgar, orpiment, K-feldspar and clays (Li-stevensite, Al-stevensite, saponite, dioctahedral smectite and illite-smectite mixed layers) are commonly associated with borate minerals (Yalçin and Gündogdu 1985 and 1987).

The Dereköy volcanics of probable upper Miocene age are represented by K-rich basaltic andesites (Semelin 1985). The Pliocene Merkezsihlar formation consists of coarse-grained detrital rocks 50 m thick, which were deposited in an alluvial environment.

Kirka basin

The northwest-trending Kirka basin is located to the south of Eskisehir (Fig. 1) and surrounded like the Bigadiç and Emet basins by Paleozoic metamorphic rocks (schist, meta-sandstone, meta-carbonate) and Eocene limestones of the Izmir-Ankara suture complex, as well as by calc-alkaline volcanics (andesites and rhyolites) of lower Miocene age (Fig. 4). The volcanic-sedimentary succession unconformably overlies these rocks and it is represented by the Karaören formation and the borate-containing Sarikaya formation of lower to middle Miocene age. It is cut by the upper Miocene Türkmendag volcanics and covered by the Fetiye formation of Pliocene age (Fig. 4).

The Karaören formation is represented by subaerial and lacustrine tuffs that are rhyodacitic-rhyolitic in composition (Yalçin 1988) and laterally transitional in the southeast (Fig. 4). Subaerial tuffs with an average thickness of 200 m, are generally white to brown in colour, non-bedded, unaltered and highly variable in grain size. They contain fibrous and porous pumice fragments (from a few mm to 15 cm in size) and quartz and biotite phenocrysts. K/Ar dating of biotites gives an average age of 17.8 Ma (Yalçin 1989) and places this unit in the uppermost part of the lower Miocene. The lacustrine facies partly including intercalations of detrital and chemical sediments, contains coarse- and fine-grained tuffs altered to zeolites and other diagenetic minerals. Coarse-grained tuffs with vitroclastic-porphyritic texture contain pumice and glass shards, feldspar (mostly andesine), biotite and small amounts of hornblende. They are classified by Yalçin (1988) as vitric or crystal tuffs and are interbedded with fine-grained tuffs that become predominant in the uppermost part of the unit. The other physical features of these tuffs are similar to the Degirmenli (Bigadiç), and the Köpenez (Emet) tuffs. Detrital intercalations from a few to 20 m in thickness are tuffaceous sandstones and tuffaceous conglomerates. They are commonly observed at the basin margin and in addition to pyrogenic material they contain epiclastic fragments of volcanic (andesite, rhyolite), metamorphic (quartzite, schist) and sedimentary rocks (limestones). In the central part of the basin, interbedded rocks make-up about 10–30% of the stratigraphic section and are mainly represented by limestones, dolomites and cherts between 1 to 10 m in thickness. These detrital and chemical intercalations indicate that explosive volcanism of Plinian type took place intermittently, as in the Emet basin.

The Sarikaya formation of middle-upper Miocene age, has an average thickness of 230 m (150 to 300 m). Clayey (claystone, marl), carbonaceous (limestone, dolomite, dolomitic limestone, cherty limestone) and siliceous rocks (chert) are the dominant lithologies in the lower and uppermost levels of this unit. It also includes borate deposits within a zone 20 to 160 m thick (mean 80 m) in the middle part. In this zone, economic borate minerals represented by borax, ulexite and colemanite, are intercalated with cm-thick clayey and tuffaceous units. Kernite, inyoite, meyerhofferite, pandermite, inderborite, kurnokovite, inderite, hydroboracite and tunellite are also locally present (Yalçin and Baysal 1991). Calcite, dolomite, strontianite, K-feldspar, quartz, opal-CT and clay minerals, such as Li-saponite, Li-stevensite and hectorite, are the main diagenetic minerals observed in this unit (Yalçin et al. 1989, 1991).

The late Miocene Türkmendag basaltic trachyandesite has a K-Ar age of 9.3 Ma (Yalçin 1989), and the Fetiye formation of Pliocene age is composed partly of reworked tuff and partly of detrital rocks of fluviatile facies.

Analytical methods

The mineralogical composition of about 1300 tuff samples, collected from surface sections and drill-cores, was determined by XRD analysis at Hacettepe University. Proportions of the minerals were calculated from the powder diffractograms using an external standard method. The relative error in this method, of which the detail is given in Temel and Gündogdu (in this issue), is less than 15%. Clay minerals were identified from three X-ray diffractograms (air-dried at 25 °C, ethylene-glycolated and heated at 490 °C for 4 h) of the clay-size fractions (<2 μm) extracted by the standard sedimentation technique in deionized water.

The thermal stability of heulandite structural group minerals, being an indicator of chemical composition (Mumpton 1960; Mason and Sand 1960; Alietti 1972; Boles 1972), was determined by using a method developed by Gündogdu (1982). In this method, which is a version of Mumpton's heating test (Mumpton 1960), the intensity (1) of the (020) reflection is measured on the same preparation before and after heating at 450 °C for 16 h, and the thermal stability is expressed as the ratio of $I_{450\ C}/I_{25\ C}$ of this reflection. This method, which allows the distinction of clinoptilolite from heulandite showing complete structural collapse after heating (Mumpton 1960; Alietti 1972; Boles 1972), enabled us to quantify thermal stability variations within the clinoptilolites.

Textures of volcanic glasses and paragenetic relations of the diagenetic minerals were examined by scanning electron microscopy (SEM) at the Centre de Géochimie de la Surface, Strasbourg and at the Université Paris-Sud, Orsay. Major element compositions of diagenetic minerals, volcanic glasses and bulk rocks were obtained by two different methods. An EDS attached to a SEM was used for volcanic glasses and diagenetic minerals. Bulk rocks and separated clinoptilolite (see Gündogdu et al. 1989 for details), together with smectite fractions were analysed by arc Spectrometry and flame photometry at Strasbourg following a method described by Besnus and Rouault (1973).

Starting materials

The starting materials of the zeolite deposits consisted mainly of fibrous pumice and porous and bubble-wall glass shards that were transformed partly into smectites during the early stage of diagenetic alteration (Fig. 5a, b). Tabular pumice fragments were also observed in the Köpenez tuffs (Semelin 1985). The geochemical data obtained from freshest tuff samples (Table 1) show that the total concentra-
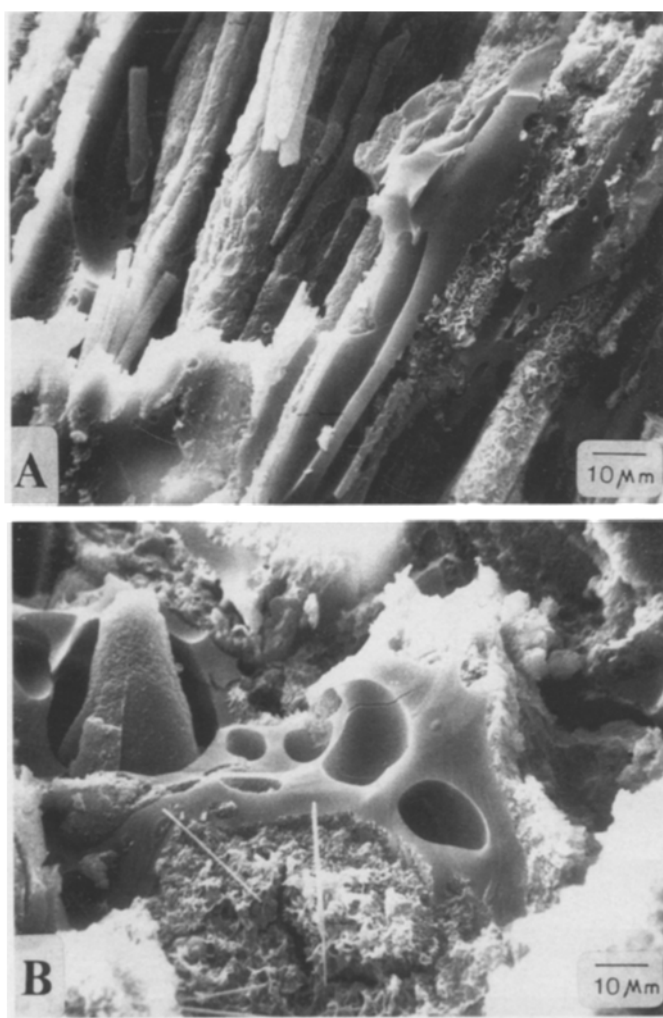
tions of the anhydrous oxide components are less than 100%. This is also the case for most glass analyses given in the literature (e.g. Broxton et al. 1987; Sheppard 1991; Rice et al. 1992; Lander and Hay 1993), and it is probably due to the hydration of the glasses after deposition (Sheppard 1991; Lander and Hay 1993). This process seems to have affected the alkali contents of the Degirmenli and Emirler glasses because their $(Na_2O + K_2O)$ values are smaller (about 1%) than the Köpenez and Karaören glasses for similar SiO_2 contents. On an anhydrous basis, the SiO_2 contents indicate that all the glasses are rhyolitic in composition. They are rich in K_2O, which varies between 4.1 and 6.9% from Degirmenli to Karaören. Na_2O is generally very low but reaches about 1.5% in some glasses in Emirler, Köpenez and Karaören. MgO (0.1–1.3%) and CaO (0.4–1.5%) contents are greater in the glass from Degirmenli.

With regard to $Si/(Al + Fe)$ ratios, the glasses of the investigated deposits are comparable to some rhyolitic glasses which were found in the USA to be precursors of zeolites. But they differ significantly from the USA glasses in their high K/Na ratios (see Table 1). This ratio varies between 3.6 and 10 in the Degirmenli, Emirler, Köpenez and Karaören, and between 0.6 and 2.3 in the USA glasses. In addition, the Degirmenli, Karaören and USA glasses contain more Fe_2O_3 than those from Köpenez and Emirler.

Zeolites and associated diagenetic minerals

Clinoptilolites and heulandites

Clinoptilolite is the most common zeolite mineral in all the deposits (Table 2). Its amount varies from 10% up to 90% and depends essentially on the vitric particle/crystal or lithoclast ratio of the tuffs. In general, the clinoptilolite contents are higher in very fine-grained tuffs than the others. The average clinoptilolite content is about 25% in crystal ash tuffs of the Degirmenli deposit and 55% in the very fine-grained tuffs forming the uppermost part of this unit. Among the deposits which consist essentially of vitric tuffs, Emirler contains about 85% of clinoptilolite and is richer than the Köpenez (60%) and Karaören (50%) deposits. This is mainly due to the relatively high crystal or

Fig. 5. A SEM photomicrographs of cylindrical pumice fibers and B porous and bubble-wall shards partly transformed into smectite

Table 1. Chemical composition of volcanic glasses (Köpenez data from Semelin 1985; Karaören data from Yalçin and Gündogdu 1992; Lake Tecopa and Barstow data from Sheppard and Gude 1968, 1969; Chalk Hills data from Sheppard 1991)

Deposit	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	MgO	CaO	Na_2O	K_2O	Total	$Si/(Al + Fe)$	K/Na
Digirmenli	70.90	13.86	1.51	0.14	0.05	1.23	1.45	1.14	4.16	94.44	4.06	2.40
Emirler	73.23	12.79	0.92	0.11	0.09	0.99	0.80	1.40	5.35	95.68	4.65	2.52
	73.66	12.38	0.71	0.02	0.05	0.49	0.39	0.99	5.29	93.98	4.87	3.52
Köpenez	70.06	13.19	0.98	0.11	0.13	0.10	0.86	0.66	6.55	92.64	4.30	6.53
	69.29	13.53	1.30	0.21	0.07	0.20	1.20	0.91	6.11	92.82	4.10	4.42
	67.68	13.19	0.97	0.06	0.12	0.11	0.86	0.84	6.66	90.49	4.16	5.22
	72.35	12.01	0.85	0.12	0.05	0.08	0.70	1.03	6.65	93.84	4.89	4.25
	69.61	13.25	0.99	0.15	0.11	0.09	0.96	1.55	6.05	92.76	4.26	2.57
	70.08	13.36	0.97	0.19	0.09	0.11	0.89	1.51	6.08	93.28	4.26	2.65
Karaören	72.22	13.92	1.34			0.79	0.87	1.31	6.19	96.64	4.15	3.11
	71.74	13.27	1.24	0.20	0.04	0.39	0.98	1.45	6.90	96.21	4.33	3.13
Lake Tecopa	72.78	11.89	1.65	0.12	0.04	0.22	0.55	3.03	5.31	95.59	4.77	1.15
Barstow	71.26	12.44	0.99	0.15	0.06	0.35	0.65	4.47	2.68	93.05	4.63	0.39
Chalk Hills	72.10	11.50	1.69	0.20	0.04	0.21	0.57	2.42	5.58	94.31	4.87	1.52

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	Degirmenli	Emirler	Köpenez	Karaören
Clinoptilolite/ Heulandite	49	93	31	16
Analcime	1	3	21	
Phillipsite				1
K-Feldspar	50	58	90	81
Clay minerals	65	10	49	43
Opal-CT	12	23	6	28
Quartz	44	50	89	88
Carbonate minerals	31	8	55	48
Number of analysed samples	390	404	181	306

lithoclast content of the Köpenez and Karaören tuffs and partially to a high K_2O content of their glasses, which caused K-feldspar formation.

Clinoptilolite associated with opal-CT, K-feldspar, quartz, analcime and smectite, completely replaced glass shards and pumice fibers as pseudomorphs, and it is commonly cryptocrystalline or massive in very fine-grained tuffs (see Fig. 2a in Gündogdu et al. 1989). Idiomorphic clinoptilolite as well-formed platy crystals 5–20 µm long and 1–3 µm thick, is only observed in the relatively large pore spaces existing within and between pyroclasts of coarse-grained tuffs (Fig. 6a–c). Clinoptilolite crystals are oriented quasi-perpendicular to the margin of the massive part from which they grew, and they formed before the opal-CT or K-feldspar crystals (Fig. 6a, c). In Fig. 6c, a part of the pore wall is made-up of platy clinoptilolite crystals and the remainder of rhomboid K-feldspars.
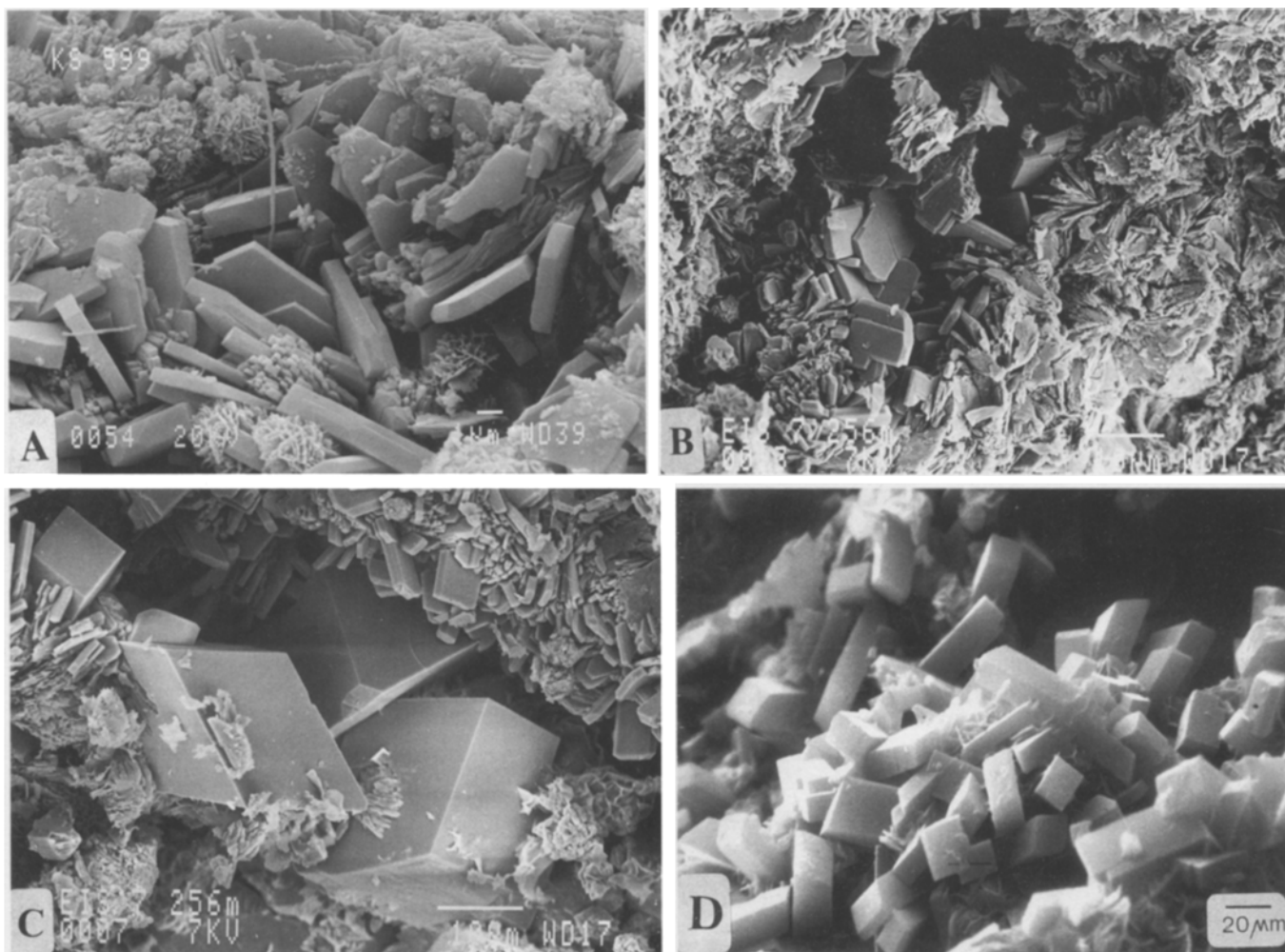

Fig. 6A–D. SEM photomicrographs of diagenetic minerals; **A** platy clinoptilolites and opal-CT balls formed of spherulites; **B** platy clinoptilolites in pore spaces surrounded by finely crystalline subhedral ones; **C** platy clinoptilolites associated with rhomboid K-feldspars in a large pore and smectite flakes covering K-feldspar in the *lower right* corner; **D** prismatic euhedral heulandites

Table 3. Average thermal stabilities (I_{450}/I_{25}-see text) of 240 clinoptilolite samples compiled from Gündogdu (1982), Yalçin (1984), Baysal et al. (1988) and Yalçin and Gündogdu (1992)

Deposit	Minimum	Maximum	Average
Degirmenli	0.06	0.65	0.20
Emirler	0.10	1.00	0.35
Köpenez	0.10	0.85	0.38
Karaören	0.25	0.80	0.40

Clinoptilolite is also observed as well-developed prismatic crystals associated with K-feldspar and analcime in very coarse-grained tuffs of the Emirler deposit (Fig. 6d). In addition, no noticeable compositional differences were found between euhedral and cryptocrystalline clinoptilolites (Gündogdu 1982; Semelin 1985; Yalçin 1988).

According to the results given in Table 3, the clinoptilolites of these deposits have different thermal stability. The average value of the ($I_{450\,°C}/I_{25\,°C}$) parameter is 0.2 in Degirmenli, 0.35 in Emirler, 0.38 in Köpenez and 0.4 in Karaören, and consequently they may be classified as the heulandite group 2 of Alietti (1972) and Boles (1972) rich in alkaline-earth elements, especially in Ca (Alietti et al. 1977).

This thermal classification is in accordance with the structural formulae of clinoptilolites given in Table 4. Their Si/(Al + Fe) ratios ranging between 4.2 and 4.9, are comparable to those of their parent materials (see Tables 1,4). Na is generally very low (0.1–0.45) as in the glasses, but it may become relatively high (0.8–1.3) in some clinoptilolites of Köpenez found with analcime and in those of the Karaören deposits (Fig. 7). Mg varies within the same range (0.4–1.1) in all the deposits (see Table 4). The

Table 4. Structural formulae (calculated on the basis of 72 oxygen atoms) and some cation ratios of clinoptilolites and heulandites (data are complied from Gündogdu 1982; Semelin 1985; Baysal et al. 1986; Gündogdu et al. 1989; Yalçin and Gündogdu 1992)

| Deposit	Si	Al	Fe	Ca	Mg	Na	K	Si/(Al+Fe)	A/AE[a]	Host rock mineralogy
Degirmenli	29.39	6.02	0.55	1.65	1.00	0.20	1.01	4.47	0.46	Clinoptilolite + opal-CT
	29.11	6.81	0.13	1.89	1.12	0.24	0.91	4.19	0.38	
	29.36	6.21	0.37	1.97	0.77	0.10	0.92	4.46	0.37	Clinoptilolite + K-feldspar + quartz
	29.21	6.22	0.57	1.60	0.95	0.19	1.24	4.30	0.56	
	28.89	6.97	0.22	2.00	1.09	0.42	0.20	4.02	0.20	Heulandite + K-feldspar + quartz
Emirler	29.19	6.48	0.33	1.57	0.72	0.04	2.19	4.29	0.97	Clinoptilolite + opal-CT
	29.52	6.18	0.16	1.26	1.04	0.07	2.15	4.66	0.97	
	29.89	5.97	0.16	0.93	0.61	0.37	2.47	4.88	1.84	
	29.84	5.99	0.13	1.39	0.65	0.07	1.99	4.88	1.01	
	29.13	6.69	0.18	1.13	1.10	0.19	2.09	4.24	1.02	
	29.6	6.06	0.22	1.35	0.84	0.15	2.11	4.71	1.03	
	29.79	5.96	0.23	1.16	0.83	0.11	2.07	4.81	1.10	
	29.57	6.24	0.22	1.95	0.73	0.14	0.76	4.58	0.34	Clinoptiolite + K-feldspar ± quartz
	29.72	6.12	0.22	1.80	0.74	0.25	0.61	4.69	0.34	
	29.75	6.08	0.19	1.87	0.77	0.18	0.48	4.74	0.25	
	29.62	6.15	0.16	1.83	0.93	0.09	0.85	4.69	0.34	
	29.63	6.10	0.19	1.82	0.81	0.15	1.08	4.71	0.47	
	29.56	6.34	0.15	1.68	0.65	0.29	1.30	4.55	0.68	
	29.89	6.05	0.06	1.45	0.92	0.45	0.89	4.89	0.57	
	29.58	6.15	0.20	1.76	0.87	0.13	1.15	4.66	0.48	
	29.39	6.59	0.13	1.84	0.75	0.25	0.86	4.37	0.43	
	29.29	6.71	0.01	2.02	1.02	0.06	0.39	4.36	0.16	Clinoptilolite + K-feldspar + analcime + quartz
Köpenez	29.25	6.52	0.16	1.59	0.64	0.31	1.89	4.38	0.99	Clinoptilolite + opal-CT
	29.4	6.38	0.04	1.97	0.93	0.39	0.58	4.58	0.33	Clinoptilolite + K-feldspar ± quartz
	29.54	6.34	0.08	2.20	0.45	0.19	0.81	4.6	0.38	
	29.88	6.04	0.03	1.71	0.76	0.29	0.78	4.92	0.43	
	29.34	6.44	0.07	1.67	0.51	1.31	0.80	4.51	0.97	Clinoptilolite + K-feldspar + analcime
Karaören	29.29	6.64	0.11	1.23	0.42	0.86	2.25	4.34	1.88	Clinoptilolite + opal-CT
	29.23	6.82	0.03	1.24	0.60	0.53	2.20	4.27	1.48	
	28.32	7.75		1.96	1.04	0.61	0.78	3.65	0.46	Heulandite + K-feldspar ± quartz
	28.63	7.29		1.58	1.22	0.73	1.28	3.93	0.72	

[a] (Na + K)/(Ca + Mg)
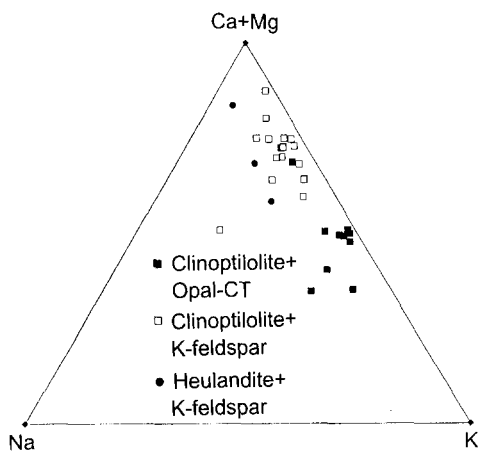
Fig. 7. Variation of exchangeable cations in clinoptilolites

amounts of K (0.48–2.25) and Ca (0.93–2.2), which are the dominant exchangeable cations, show a large variation (see Fig. 7). The alkali/alkaline-earth (A/AE) ratios of the clinoptilolites, ranging between 0.16 and 1.88, are thus mainly controlled by these two cations. The average values of the A/AE ratios increase from Degirmenli to Karaören, as do the average thermal stabilities (see Tables 3,4). This relationship may indicate that the thermal stabilities of clinoptilolites are governed by the alkali element content of the channels, especially by K, as concluded by several other authors (e.g. Mason and Sand 1960; Alietti 1972; Boles 1972; Alberti 1975; Alietti et al. 1977; Barrows 1980; Gündogdu 1982; Gündogdu and Ataman 1984; Semelin 1985; Yalçin and Gündogdu 1992). In addition, a close relationship is observed between the channel compositions of clinoptilolites and the mineralogical compositions of the samples. For example, in the Emirler, Köpenez and Karaören deposits, clinoptilolites associated with opal-CT, have a high K content (1.89–2.25), while those rich in Ca (1.45–2.2) are found with K-feldspar or K-feldspar + analcime. However, this is not the case in the Degirmenli deposits where Ca-clinoptilolites are associated with K-feldspar or opal-CT (see Fig. 7). The Ca-rich group of the Köpenez deposit was classified as heulandite by Semelin (1985), but it should be termed clinoptilolite because this group is not different from the K-rich group with respect to Si/(Al + Fe) ratios (see Table 4). Moreover, the structural collapse considered as the major thermal characteristic of heulandite (Mumpton 1960; Alietti 1972 and Boles 1972) was never observed in the samples of this group (Yalçin 1984; Semelin 1985).

Heulandites showing a complete structural collapse in the heating test, were found in some samples of the crystal ash tuffs of the Degirmenli and Karaören deposits. They are also closely associated with authigenic K-feldspar as Ca-clinoptilolites. The same association was first reported by Boles and Surdam (1979) from sandy volcaniclastic units of lacustrine Wagon Bed Formation. The Degirmenli and Karaören heulandites are richer in Na compared to the Ca-clinoptilolites of these deposits (see Fig. 7). Their A/AE ratios are similar to those of Ca-clinop-

tilolites, but their Si/(Al + Fe) ratios are less than 4.02 (see Table 4). The Karaören heulandites were also observed as prismatic crystals (Yalçin and Gündogdu 1992), as was Ca-clinoptilolite associated with K-feldspar + analcime in the Emirler deposit (see Fig. 6d). Therefore, as already claimed by Yalçin and Gündogdu (1992), it may be suggested that the crystal morphologies of heulandite group minerals appear to have been controlled by their chemical compositions.

Analcimes

Analcimes are found more frequently in the Köpenez deposit of Emet than in the Emirler and Degirmenli tuffs of Bigadiç, and they are never observed in the Karaören deposit of Kirka (Table 2). They exist only in the K-feldspar-bearing coarse-grained tuffs where they are commonly associated with quartz and clay minerals and rarely with clinoptilolite (Köpenez and Emirler). Their quantities range from a trace up to 30% and their modes of formation are very similar to those of clinoptilolites. Cryptocrystalline analcime pseudomorphing pumice and glass shards are the most common occurrences, as was reported from Yucca Mountain, Nevada (Broxton et al. 1987). Subhedral to euhedral analcime crystals of large size (20–40 µm) are observed only in relatively large pore spaces where the crystal shape or growth of analcime was disturbed by K-feldspar crystals (Fig. 8a). A similar relation between these two minerals may also be seen in a photomicrograph of a tuff near Barstow, California (see Fig. 29 in Mumpton and Ormsby 1978). In a Na-clinoptilolite-analcime association found in the Köpenez deposit, one of two adjoining pore spaces was filled up with platy clinoptilolite and the other with globular analcime crystals partially covered by smectite (Semelin 1985). These relations indicate that the analcime succeeded the idiomorphic K-feldspars and that there is no diagenetic transformation between analcime and clinoptilolite or K-feldspar.

The average structural formulae listed in Table 5 demonstrate that the analcimes associated with K-feldspar, quartz and clay minerals in the Emirler and Köpenez deposits, have high Si/Al ratios of about 2.6. On the basis of this ratio, they are comparable to other analcimes observed in diagenetically altered silicic tuffs (e.g. Sheppard and Gude 1969, 1973; Moncure et al. 1981; Ratterdam and Surdam 1981; Ataman and Gündogdu 1982; Broxton et al. 1987) and may be classified as Group A analcime of Coombs and Whetten (1967). In addition, analcime obtained from the experimental alteration of Lake Tecopa rhyolitic glass, exhibits practically the same Si/Al ratio (about 2.7; Barth-Wirsching and Höller 1989).

Phillipsites

Phillipsites associated with K-feldspar + smectite + calcite are found only in some samples from the Karaören deposit (Yalçin et al. 1991). They make-up about 20% of the rocks and are observed as prismatic and
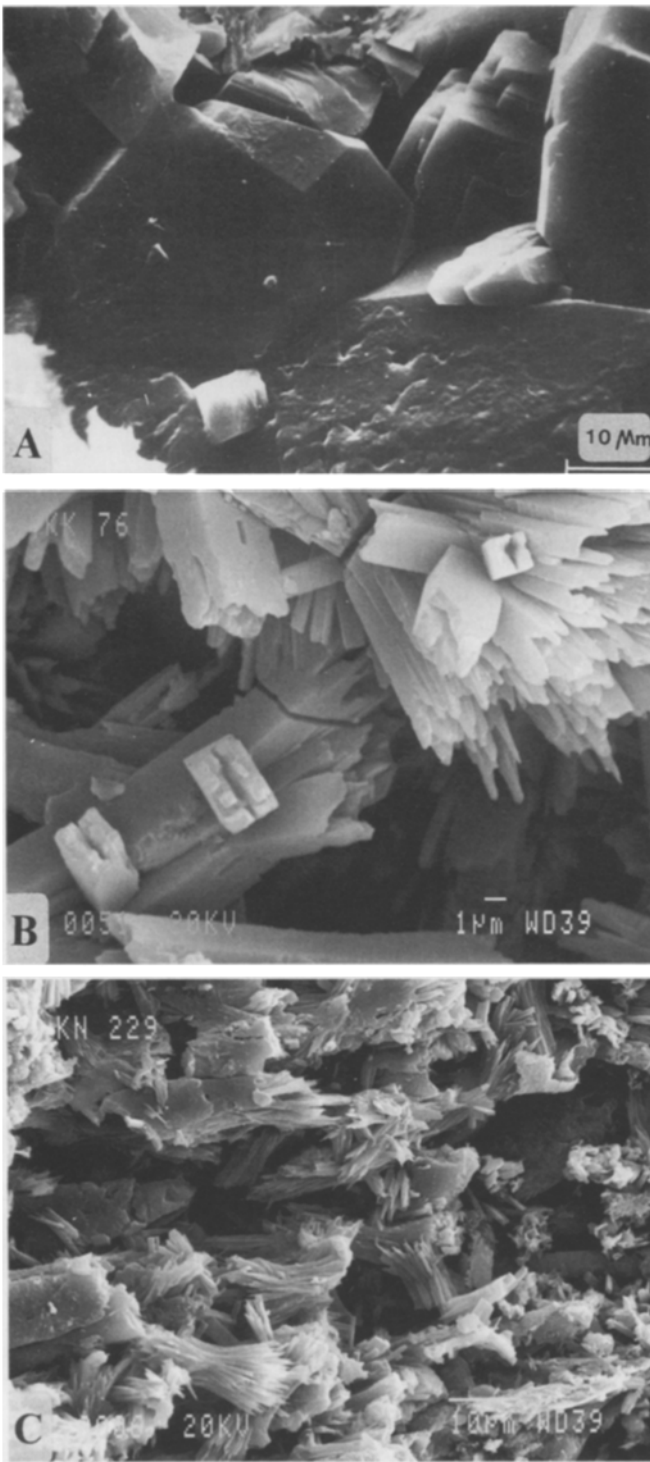
Ormsby 1978), crystals become smaller. Acicular/ fibrous phillipsites (20 µm long) form crystal bunches which are flattened in the middle and widened towards the edges (Fig. 8c).

These two types of phillipsite containing Na as the dominant cation, are also different in their Si/Al ratios and exchangeable cation contents (see Table 5). Prismatic philipsites have low Si/Al ratios (1.95) and high Ca contents (1.38), whereas acicular/fibrous ones contain relatively low Ca (0.73), which is compensated by higher Si/Al ratios (2.4), as well as K and Mg contents. Thus, the crystal morphology of phillipsite seems also to be controlled by its chemical composition, as is the case for the heulandite group minerals (Yalçin and Gündogdu 1992). In addition, the Karaören phillipsites are rather different from other lacustrine phillipsites that have been found in silicic tuffs that are characterized by high Si/Al ratios (between 3 and 3.4) and very low Ca contents (e.g. Hay 1964; Sheppard and Gude 1968, 1969, 1973; Taylor and Surdam 1981; Sheppard and Fitzpatrick 1989; Sheppard 1991).

K-feldspars

K-feldspars are especially common and abundant in the Köpenez and Karaören deposits where the glasses contain relatively high K_2O (see Table 2). The average amounts of K-feldspar are about 10 to 40%, and are generally low in the Ca-clinoptilolitic tuffs. K-feldspar commonly occurs as cryptocrystalline pseudomorphs after pumice and glass shards, or as euhedral crystals in the pores, and rarely as overgrowth around pyrogenic feldspars (Gündogdu 1982; Yalçin 1984, 1988; Semelin 1985). It is associated with each of the other diagenetic minerals except K-clinoptilolite and it is observed as rhomboid or twinned crystals in the cavities of medium- to coarse-grained tuffs (Figs. 6c, 9a). The association of euhedral K-feldspar with coarse grained volcaniclastics was also observed in other lacustrine (Boles and Surdam 1979) and marine environments (Kastner and Siever 1979). In the clinoptilolite-rich tuffs, simple or twinned K-feldspar crystals which seem to have grown from cryptocrystalline ones (Fig. 9a), succeed Ca-clinoptilolite and precede smectite (Fig. 6c), whereas they precede analcime (Fig. 8a), quartz (Fig. 9b) and smectite (Fig. 9c) in the analcime-bearing tuffs. In Fig. 9a, a small pore in a glass shard is partly occupied by platy clinoptilolite crystals, while K-feldspar crystals become dominant in an adjoining large pore space. The same relations have also been observed between K-feldspar and ferrierite, another silica-rich zeolite, in rhyolitic tuffs where K-feldspar appears to have been formed after ferrierite (Rice et al. 1992).

The associations of K-feldspar with smectite + quartz or with opal-CT are commonly observed in non-zeolitic tuffs of the Köpenez and Karaören deposits, respectively (Semelin 1985; Yalçin and Gündogdu 1987; Yalçin 1988). In the Köpenez deposit, the rhomboid K-feldspar crystals were also succeeded by quartz and smectite (Semelin 1985; Yalçin and Gündogdu 1992), as in the analcime-bearing tuffs (see Fig. 9b, c). Prismatic K-feldspar crystals associated with opal-CT in the Karaören tuffs are generally perpendicular to each other and uniformly oriented

Fig. 8A–C. SEM photomicrographs of diagenetic minerals. **A** euhedral, trapezohedral analcime, prismatic K-feldspar and trigonal quartz; **B** prismatic phillipsites; **C** bunches of fibrous phillipsite

acicular/fibrous crystals in the pore spaces (Yalçin and Gündogdu 1992). Prismatic phillipsite crystals, 10–15 µm long and 3–5 µm thick, occur in rosettes or radial clusters and have cracks which are parallel to the c-axis (Fig. 8b). As a result of breakage, which is a characteristic of pseudo-orthorhombic phillipsites (Mumpton and

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Mineral	Deposit	Si	Al	Fe	Ca	Mg	Na	K	Si/Al	Associated diagenetic minerals
Analcime	Emirler	34.39	13.60	0.02	0.05		13.25		2.53	K-feldspar + Ca-clinoptilolite + quartz + smectite
		34.80	13.11	0.03	0.01		12.85	0.08	2.65	
		34.31	13.64				13.70		2.52	
	Köpenez	34.93	13.05	0.05	0.02		12.69	0.06	2.68	K-feldspar + smectite + (I-S) + quartz
		34.88	12.92	0.04	0.02		12.88	0.20	2.70	
		35.04	13.01	0.01	0.01		12.69	0.01	2.70	
Phillipsite	Karaören	10.60	5.43	0.04	1.38	0.15	1.90	0.23	1.95	K-feldspar + smectite + calcite
		11.20	4.53	0.19	0.73	0.35	1.90	0.74	2.47	
K-Feldspar	Emirler	3.04	0.90					0.90	3.38	Ca-clinoptilolite + quartz
		3.05	0.93					0.95	3.28	Analcime + Ca-clinoptilolite + quartz + smectite
		3.04	0.93					0.95	3.27	
	Köpenez	3.09	0.90					0.93	3.43	Ca-clinoptilolite + quartz
		3.07	0.93					0.88	3.30	
		3.04	0.91					0.95	3.34	Analcime + smectite + (I-S) + quartz
		3.04	0.91					0.85	3.34	Smectite + quartz

[a]Calculated on the basis of 96 oxygen atoms for analcimes, 32 for phillipsites and 8 for K-feldspars

(Fig. 9d). In addition, in some coarse-grained samples from this deposit, K-feldspar is also observed with relict glass. The very small sub- to euhedral K-feldspar crystals (1–2 μm in size) pseudomorph the glass (Fig. 10a), or grow on its etched surface with smectite of corn-flake texture (Fig. 10b). These SEM data clearly demonstrate that K-feldspars have been formed directly from the glass shards, as observed by Kastner and Siever (1979) in a marine environment. They also prove that no diagenetic transformation exists between clinoptilolite and K-feldspar.

The chemical compositions of K-feldspars listed in Table 5 indicate that their Si/Al ratios are nearly constant (about 3.3) in all mineralogical associations and high relative to that of the ideal feldspar formula. Similar Si-rich K-feldspars formed from silicic volcanic glass were reported by Broxton et al. (1987) and Rice et al. (1992).

Clay minerals

The clay minerals are mainly represented by dioctahedral smectites. They are observed most commonly in Degirmenli, Köpenez and Karaören, where the glass + smectite zones cover relatively large areas (see Table 2). Their amounts are low in clinoptilolite-rich tuffs and high in samples containing K-feldspar + analcime. A similar negative relationship between clinoptilolite and smectite has already been noted by some other authors (e.g. Sheppard and Gude 1968; Papke 1972; Sheppard 1991). Smectites representing the early stage of diagenetic alteration in the glass + smectite assemblage, are generally observed along the pumice fibers or at the outer margin of porous glass shards (see Fig. 5a, b). The are also considered by some authors as the first minerals in different mineralogical assemblages developed during diagenesis of silicic tuffs (e.g. Sheppard and Gude 1968, 1969, 1973; Sheppard

1991). However, their relations with other minerals that have been described above, suggest that smectites are more probably the latest phases in the tuffs completely altered during diagenesis, as concluded by Rice et al. (1992). Small amounts of illite-smectite mixed-layers (I/S) developed from smectite particles (Semelin 1985), are only observed in K-feldspar-analcime-quartz bearing tuffs of Köpenez (Yalçin 1984; Semelin 1985).

The structural formulae of dioctahedral smectites are presented in Table 6. Some smectites found with glasses or clinoptilolites contain excess Si or K because of the existence of very fine-grained opal-CT, quartz or K-feldspar. These dioctahedral smectites are montmorillonite or beidellite with respect to their tetrahedral Al substitutions (Gündogdu 1982; Semelin 1985; Yalçin and Gündogdu 1985, 1987; Yalçin et al. 1991). In particular, octahedral Mg varies within a narrow range in all smectites except one sample from the Emirler deposit with K-feldspar + analcime + Ca-clinoptilolite. The montmorillonitic smectites with low tetrahedral Al content are associated with fresh glasses. In contrast, the beidellitic smectites with relatively high tetrahedral substitutions occur in the zeolite- or K-feldspar-bearing tuffs and are richer in Fe in the analcimic ones. In addition, the montmorillonitic smectites of the Degirmenli and Karaören deposits are richer in Fe than those of the Emirler and Köpenez tuffs, similar to the glasses. This is also the case for beidellitic smectites associated with K-feldspar in Köpenez and Karaören (see Tables 1, 6). The exchangeable cations are dominated by Ca and Mg in all the smectites.

Opal-CT and quartz

Opal-CT associated with K-clinoptilolite in the fine-grained tuffs in all deposits, or with K-feldspar in the coarse-grained
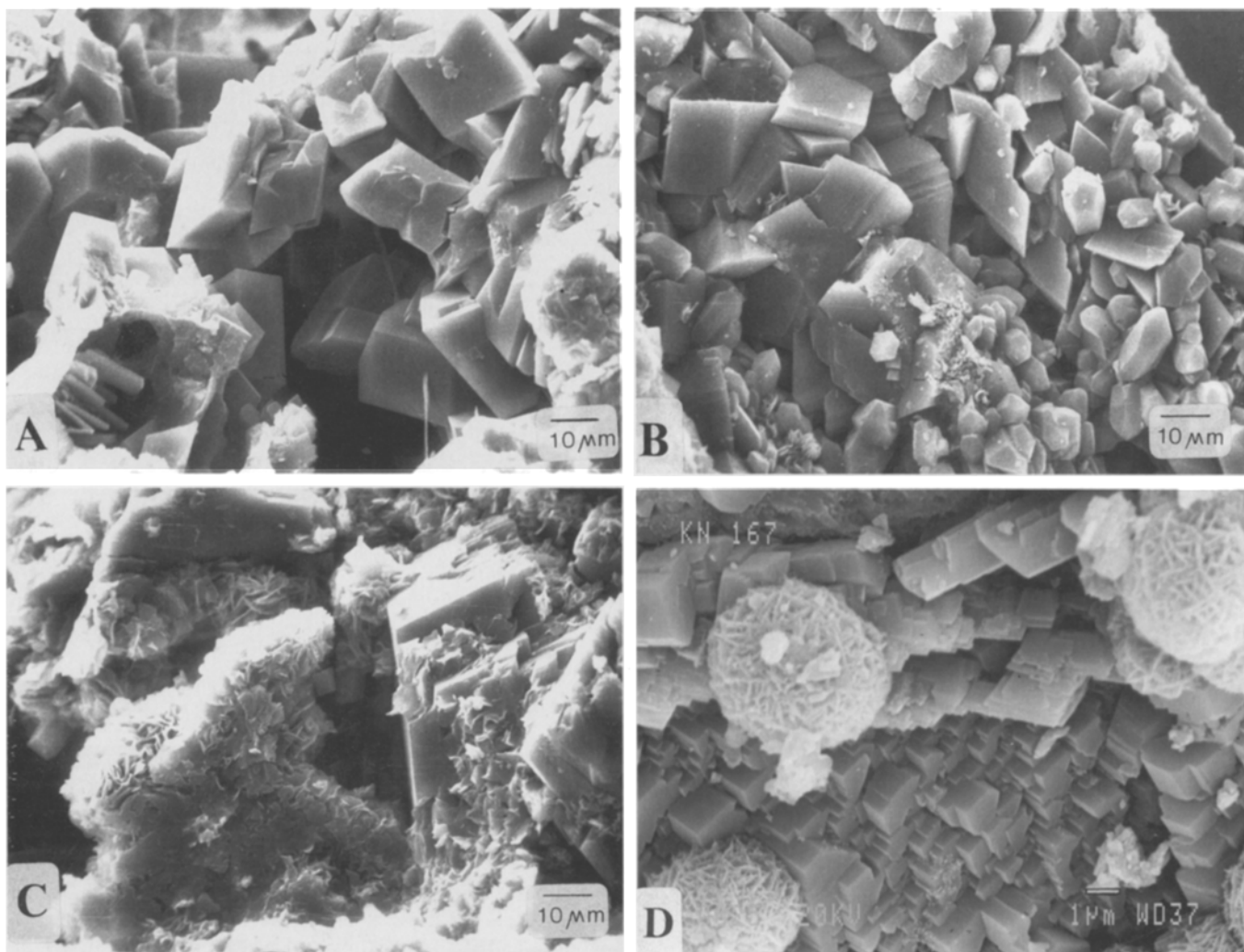
Fig. 9A–D. SEM photomicrographs of diagenetic minerals. **A** K-feldspars with Carlsbad and pericline twinnings and platy clinoptilolite partly filling the cavities in the *lower left* corner; **B** hexagonal bi-pyramidal quartz overgrown on prismatic K-feldspars; **C** K-feldspars coated by smectite flakes; **D** prismatic K-feldspars uniformly oriented and individual balls of opal-CT

tuffs in the Karaören deposit, occurs as spherules which were formed by the combination of minute crystals smaller than 1 μm (see Figs. 6a, 9d). The individual opal-CT spherules have a diameter of about 10 μm and seem to be perched on K-feldspar crystals, as observed between clinoptilolite and opal-CT by Moncure et al. (1981). Idiomorphic quartz crystals, as 5–20 μm hexagonal bipyramids, are only observed in K-feldspar dominated associations, where they are overgrown on K-feldspars (see Fig. 9b) or intergrown with smectites in the groundmass of tuffs. In all deposits, opal-CT is less common than quartz (see Table 2), and it is found in Ca-clinoptilolite or K-feldspar dominated mineral assemblages. The amount of these silica minerals, which are the latest minerals to form in clinoptilolite-dominated assemblages, is less than 20%. However, quartz becomes especially important in K-feldspar-dominated associations (up to 40%). In the zeolitized tuffs of the Köpenez and Emirler deposits, the silica-rich hydrated granules with opal-CT-like morphology are also observed in the K-clinoptilolite + opal-CT facies and

contain Al_2O_3 and K_2O (Gündogdu 1982; Semelin 1985). According to the chemical analyses carried out by Semelin (1985), the Al/K ratios of these granules are about 1.2 and higher than those of K-feldspars (Table 7).

Carbonate minerals

The carbonate minerals observed as cement, are commonly calcite and rarely dolomite. In all the deposits investigated, calcite is common in the slightly altered tuffs containing fresh glass + smectite, as well as in K-feldspar-dominated mineralogical associations. As a consequence, it is most frequently found in the Karaören, Köpenez and Degirmenli deposits, where the glass + smectite and K-feldspar-dominated associations cover relatively large areas (Table 2). Within the tuffs containing clinoptilolite, as the dominant diagenetic mineral, calcite is absent in the vitric tuffs rich in clinoptilolite but it is occasionally present in the clinoptilolite-poor crystal tuffs. Similar inverse
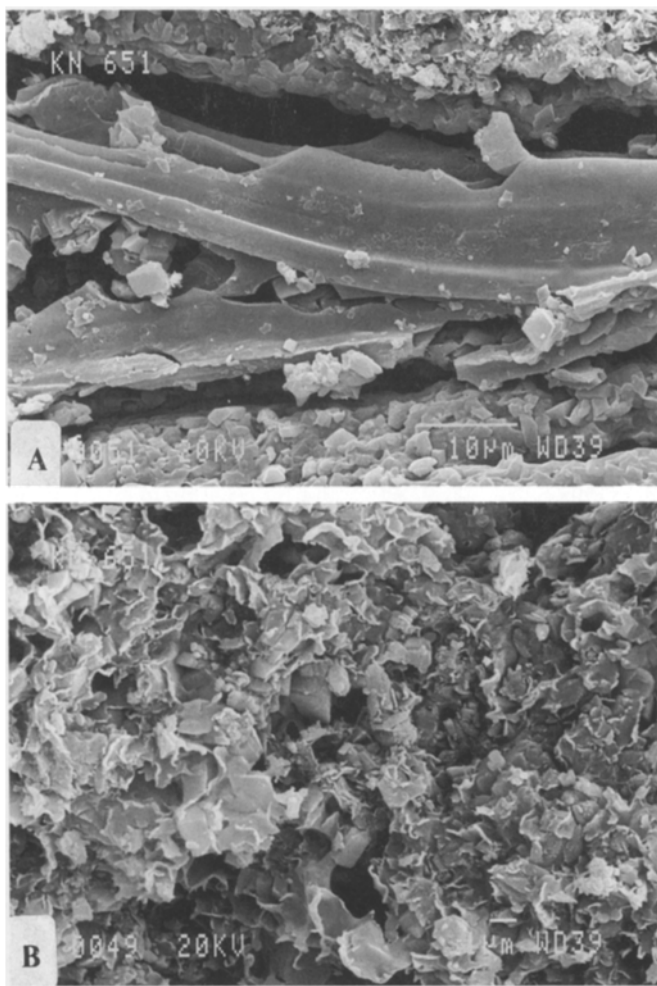
Fig. 10A, B. SEM photomicrographs of diagenetic minerals. **A** sub- and euhedral K-feldspar on volcanic glass surface; **B** the enlarged appearance of the glass surface in **A** where K-feldspars are intergrown with smectite with cornflake texture

Table 7. Chemical composition of granules observed in the K-clinoptilolite + opal-CT facies of Köpenez deposit (data from Semelin 1985)

SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	Na$_2$O	K$_2$O	H$_2$O[a]	Al/K
87.57	5.4	0.27	0.37	3.92	2.37	1.27
85.75	6.33	0.44	0.24	5.14	1.72	1.14
85.19	6.34	0.63	0.19	4.83	2.3	1.21
81.92	7.78	0.24	0.59	5.69	3.43	1.26
84.71	6.04	0.24	0.26	4.84	3.68	1.15
83.06	6.76	0.24	0.18	5.09	4.2	1.23

[a] H$_2$O obtained by difference

relation between calcite and heulandite-group zeolites have been reported from volcanigenic materials diagenetically altered in various hydrologic systems (Boles and Surdam 1979; Barrows 1980; Broxton et al. 1987; Münch and Cochemé 1993). Dolomite is also generally related to glass + smectite or K-feldspar-dominated mineralogical associations. These observations indicate that the formation of calcite or dolomite probably occurred when Ca and Mg were not consumed by heulandite/clinoptilolite or clay minerals.

Diagenetic facies and their distributions

Beside the glass + smectite association which represents the early stage of diagenetic alteration of vitreous materials, the main diagenetic mineral facies observed in the deposits investigated are generally dominated by clinoptilolite and K-feldspar. Tuffs are dominant in the uppermost part of the sections in all deposits. The lateral distributions of these facies are shown in the zoning maps, where the outcrops of tuffs and basement rocks surrounding the basins, are also presented (Figs. 11, 12, 13, 14). The facies boundaries were established by using the XRD data

Table 6. Structural formulae of representative smectites, calculated on the basis of 11 oxygen atoms (Köpenez and Karaören data from Semelin 1985; Yalçin et al. 1991)

| Deposit	Si	Al^{IV}	Al^{VI}	Fe	Mg	Mg	Ca	Na	K	Other phases
Degirmenli	4.09		1.38	0.11	0.38		0.17	0.01	0.04	glass
	3.90	0.10	1.62	0.10	0.28	0.14	0.06	0.01	0.01	
	4.07		1.15	0.21	0.32		0.14	0.12	0.47	Ca-clinoptilolite + K-feldspar + quartz
	4.08		1.14	0.27	0.3		0.08	0.01	0.37	
Emirler	4.16		1.18	0.07	0.43		0.26	0.04	0.05	glass
	3.73	0.27	0.96	0.34	0.97		0.2	0.02	0.01	K-feldspar + analcime + Ca-clinoptilolite
Köpenez	4.10		1.40	0.08	0.33		0.12	0.05	0.07	glass
	4.10		1.53	0.12	0.16		0.11		0.09	K-clinoptilolite + opal-CT
	3.89	0.11	1.41	0.35	0.24	0.02	0.13	0.04		Ca-clinoptilolite + K-feldspar + quartz
	3.87	0.13	1.31	0.45	0.24	0.14	0.04			
	3.83	0.17	1.28	0.40	0.32	0.18	0.06	0.02		
	3.77	0.23	1.20	0.58	0.22	0.09	0.09	0.09		Ca-clinoptilolite + K-feldspar + analcime
	3.88	0.12	1.61	0.08	0.29		0.22		0.02	K-feldspar + quartz
	3.86	0.14	1.61	0.09	0.25		0.24		0.06	
	3.89	0.11	1.63	0.06	0.31	0.01	0.19		0.03	
Karaören	3.93	0.07	1.50	0.16	0.34		0.15	0.01	0.11	glass
	3.86	0.13	1.53	0.22	0.25	0.08	0.07	0.01	0.07	K-feldspar + glass
	3.77	0.23	1.21	0.53	0.26	0.05	0.17	0.01	0.07	
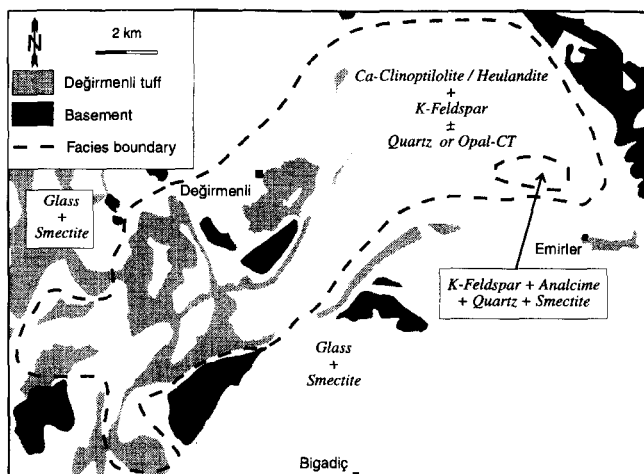
Fig. 11. Outcrop and diagenetic facies map of the Degirmenli deposit of the Bigadiç basin (prepared from data obtained by Gündogdu 1982; Baysal et al. 1986; Temel 1987)
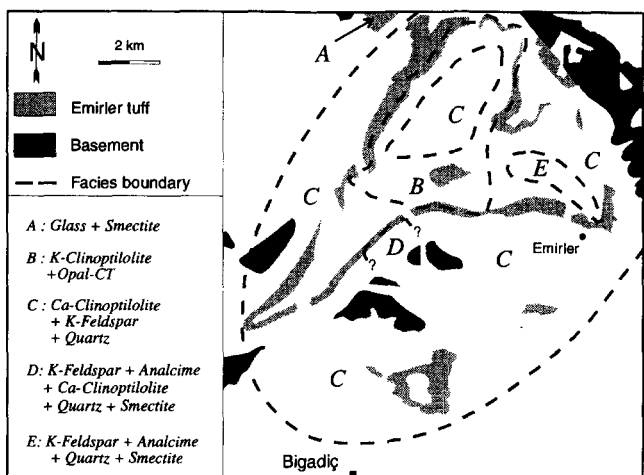

Fig. 12. Outcrop and diagenetic facies map of the Emirler deposit of the Bigadiç basin (prepared from data obtained by Gündogdu 1982; Baysal et al. 1986; Temel 1987)

Fig. 13. Outcrop and diagenetic facies map of the Köpenez deposit of the Emet basin (modified from Semelin 1985; Yalçin and Gündogdu 1987)

Fig. 14. Outcrop and diagenetic facies map of the Karaören deposit of the Kirka basin (modified from Yalçin et al. 1991)

of whole-rock samples collected mainly from surface sections. The results of drill-core samples were also used for the Degirmenli, Emirler and Karaören deposits.

In the Degirmenli deposit of the Bigadiç basin, a lateral diagenetic facies zoning is observed between (glass + smectite + calcite), (Ca-clinoptilolite/heulandite + K-feldspar ± quartz/opal-CT ± smectite) and (K-feldspar + analcime + smectite + quartz) associations. This zoning extends from northeast to southwest in accordance with the trend of the basin (Fig. 11). The Ca-clinoptilolite/heulandite-dominated facies is surrounded by glass + smectite in the southwest and covers a broad area in the central part of the basin. The K-feldspar + analcime association is identified by means of drill-core samples as a narrow zone in the clinoptilolite/heulandite-dominated facies in the northeastern part of the area.

In the Emirler deposit of the Bigadiç basin, diagenetic facies are represented by (glass + smectite), (K-clinoptilolite + opal-CT), (Ca-clinoptilolite + K-feldspar ± quartz), (K-feldspar + analcime + Ca-clinoptilolite +
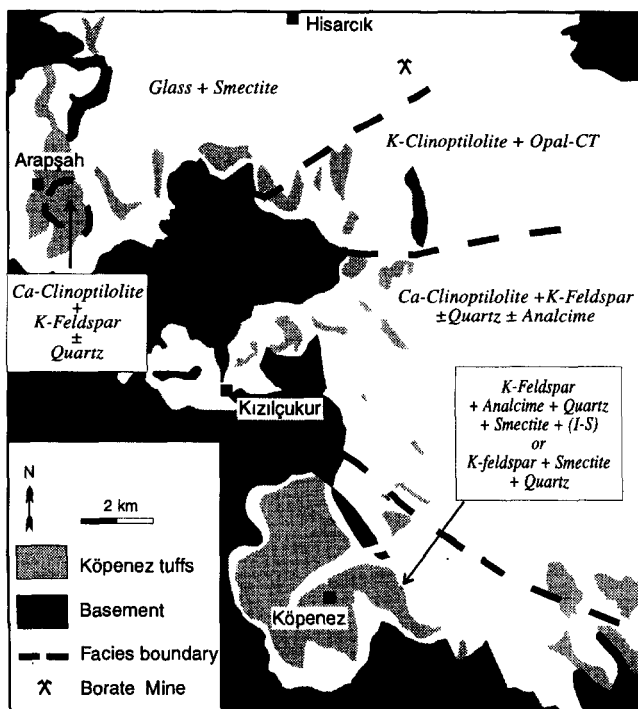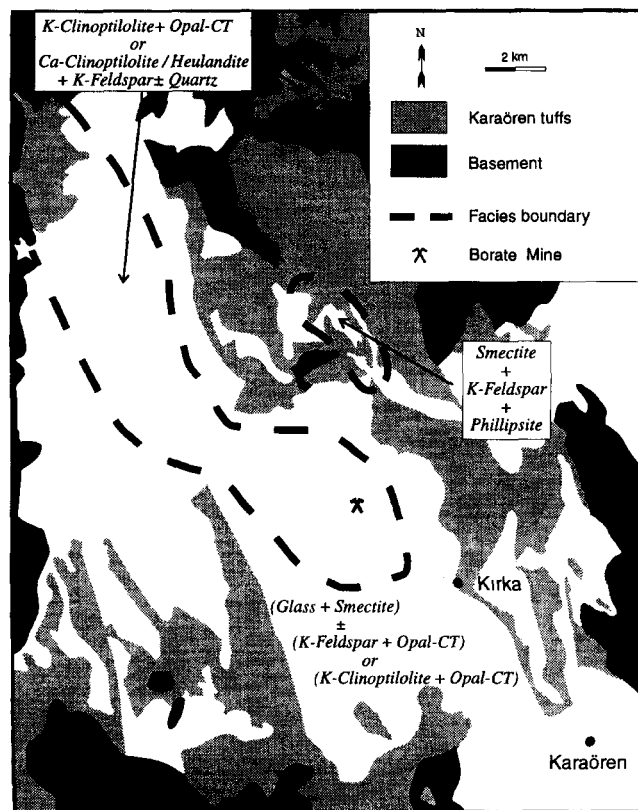
quartz + smectite) and (K-feldspar + analcime + quartz + smectite) associations (Fig. 12). Some vertical zonations related to the grain-size of tuffs are observed between these facies. In the northwestern part of the basin, the K-clinoptilolite + opal-CT facies is found in the very fine-grained tuffs, whereas Ca-clinoptilolite is dominant in the coarse-grained tuffs. The K-clinoptilolite dominated facies passes laterally into the Ca-clinoptilolite + K-feldspar ± quartz facies. The effect of grain size disappears in the central part of the three borate-bearing sub-basins, which developed as a result of synsedimentary extensional tectonics (Temel 1987). Another vertical zonation, also related to grain size, is locally found within the Ca-clinoptilolite facies in the central part of the study area where the very coarse-grained tuffs containing K-feldspar + analcime + Ca-clinoptilolite are overlain by tuffs containing Ca-clinoptilolite + K-feldspar. The K-feldspar + analcime + smectite + quartz facies is only found in the northeastern part of the basin in the Degirmenli deposit.

In the Köpenez deposit that outcrops near the western and southern borders of the Emet basin, a lateral diagenetic facies zoning is observed from northwest to southeast between (glass + smectite), (K-clinoptilolite + opal-CT), (Ca-clinoptilolite + K-feldspar ± quartz ± analcime) and (K-feldspar + analcime + quartz + smectite + I/S mixed layers) or (K-feldspar + smectite + quartz) associations (Fig. 13). In addition, a paragenesis of Ca-clinoptilolite + K-feldspar ± quartz is developed within the glass + smectite facies in the Arapsah area (see Fig. 13). This lateral zoning can only be confirmed for the upper and middle parts of this deposit because the lower part is never observed except in one section in the southwest. According to the data of Yalçin (1984) and Yalçin and Gündogdu (1987), some particular vertical variations depending on the grain size and composition of the tuffs exist between the diagenetic facies. For example, the analcime-containing Ca-clinoptilolite or K-feldspar dominated facies are related to coarse grained tuffs and interbedded with analcime-free medium- to fine-grained tuffs. The K-feldspar + smectite + quartz facies is found in crystal tuffs in the southeastern part of the basin.

In the Kirka basin, the most important mineralogical facies are (glass + smectite), (K-clinoptilolite + opal-CT) or (Ca-clinoptilolite/heulandite + K-feldspar ± quartz). The glass + smectite facies which is generally dominated by smectite, covers a large area and locally contains K-feldspar + opal-CT in coarse-grained tuffs or K-clinoptilolite + opal-CT in medium- to fine-grained tuffs. This mineralogical difference related to the grain size of the tuffs is also valid for the K- and Ca-clinoptilolite/heulandite dominated facies. As a consequence, these two facies are intercalated in the central part of the Kirka basin, where they are surrounded by the glass + smectite facies, and in a small basin located in the northern part of the study area (Fig. 14). The smectite + K-feldspar + phillipsite association is found in a small area within the glass + smectite facies.

The lateral facies zoning observed in the Emirler, Degirmenli and Karaören deposits, such as the change from glass + smectite to clinoptilolite and to K-feldspar dominated associations from the border to the centre of the basin, are generally concentric and partly similar to those reported by Sheppard and co-authors (Sheppard and Gude 1968, 1969, 1973; Surdam and Sheppard 1978; Sheppard 1991). Therefore, they may be interpreted as the result of formation in closed hydrological systems where the pH, total salinity and alkali/alkaline-earth ratio of lake waters increased toward the central part of the basins (Jones 1965; Eugster and Jones 1979). These distributions, especially that observed in the Karaören deposit, may indicate that the paleolakes were fed by a fresh-water influx from all directions. The existence of tuffaceous sandstone and conglomerate intercalations in the marginal part of the Karaören deposit supports this interpretation.

In the Köpenez deposits of the Emet basin, the lateral facies zoning developed from northwest to southeast, is rather different from the others, and the facies boundaries are not parallel to the basin margin. The development of different diagenetic facies even in the very fine-grained tuffs of the upper part of the succession, excludes the effect of grain size which increases in coarse-grained tuffs in the same direction. There is also a similarity between the distribution of diagenetic facies and depositional environments in the clastic sediments of the Beyköy formation situated above the Köpenez tuffs. In other words, the glass + smectite and clinoptilolite- or K-feldspar-dominated facies globally correspond to the fluvial and lacustrine environments, respectively (Semelin 1985; Yalçin and Gündogdu 1985, 1987). By taking into consideration only this relation, Semelin (1985) proposed that the diagenesis of the tuffs occurred during the deposition of the Beyköy formation. However, this idea implying an open hydrological system seems to be unrealistic, because a thick laminated limestone (60 m) separates the tuffs from the clastics under consideration. In addition, the tuffs are only interbedded with the same type of limestones and contain no epiclastic intercalations even at the basin margin. This clearly indicates that the environmental conditions suitable for carbonate precipitation were maintained during deposition of the tuffs. Therefore, the diagenetic distribution pattern observed in the Köpenez deposit can also be related to a closed hydrologic system, which was chemically zoned from northwest to southeast. The organic-matter-rich laminated limestones existing in the Dogankayasi formation and the Köpenez tuffs in the southern part of the basin may indicate that the Emet paleolake was more confined in this area before and during deposition of the Köpenez deposits. Similar relationships between authigenic mineral occurrences and depositional environment have previously been described by a number of workers (e.g. Hay 1966; Sheppard and Gude 1968, 1969, 1973; Surdam and Parker 1972; Surdam and Sheppard 1978; Boles and Surdam 1979).

Chemistry of tuffs

Bulk chemical analyses of vitric tuffs representing different diagenetic facies in the Emirler and Köpenez deposits are given in Table 8. On an anhydrous basis, the compositions of tuffs in the glass + smectite and zeolite facies are similar, except for alkali and alkaline-earth element contents. The samples from the clinoptilolite + opal-CT facies are richer in K_2O than those of the clinoptilolite + K-feldspar

Table 8. Chemical composition (recalculated on an anhydrous basis) of tuffs representing different diagenetic facies of the Emirler and Köpenez deposits (Köpenez data from Semelin 1985)

Deposit	Mineralogy	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	TiO$_2$	MgO	CaO	Na$_2$O	K$_2$O
Emirler	glass + smectite + calcite	73.94	13.51	1.55	0.01	1.45	2.81	1.24	5.47
		72.36	13.89	2.10	0.03	2.13	3.16	1.11	5.17
	K-clinoptilolite + opal-CT	77.31	13.48	0.86	0.11	1.55	3.56	0.18	2.94
		77.68	12.62	1.52	0.08	1.58	3.15	0.17	3.19
		77.57	13.00	1.08	0.09	1.44	3.79	0.57	2.44
	Ca-clinoptilolite + K-feldspar	79.11	12.75	0.54	0.09	1.08	3.92	0.31	2.19
	± quartz	77.22	13.66	1.21	0.10	1.48	3.97	0.39	1.88
		77.56	13.78	0.08	0.09	1.53	4.11	0.24	2.60
		78.62	13.12	0.67	0.09	1.29	4.56	0.32	1.32
	K-feldspar + analcime	77.78	11.83	1.15	0.07	1.28	0.52	3.27	4.07
	+ Ca-clinoptilolite + quartz	78.26	12.14	1.14	0.06	0.91	0.06	2.78	4.60
	+ smectite	74.02	13.48	1.37	0.08	2.20	0.74	4.12	3.98
Köpenez	glass + smectite	75.72	13.86	1.76	0.22	0.60	1.38	1.22	5.23
	K-clinoptilolite + opal-CT	76.15	14.02	1.56	0.24	0.97	2.48	0.64	3.94
	Ca-clinoptilolite + K-feldspar ± quartz	75.67	14.31	1.49	0.23	1.10	4.12	0.27	2.81
	K-feldspar + analcime + smectite + (I-S) + quartz	77.97	11.55	0.83	0.18	0.25	1.46	2.7	5.07

facies. Na$_2$O becomes important in the analcime-bearing facies, but never exceeds K$_2$O except for one sample from Emirler.

For the purpose of inferring chemical variations during the diagenesis of vitric material, the compositions of the fresh glasses and diagenetic facies were compared with regard to their SiO$_2$, alkali and alkaline-earth elements. Oxide ratios were used in these comparisons. Al and Fe oxides were assumed to be immobile during alteration of volcanic glasses because of their low solubility, and their sum was taken as the denominator.

The comparison between the major components of the tuffs indicates that the SiO$_2$/(Al$_2$O$_3$ + Fe$_2$O$_3$) ratios of the glass + smectite and clinoptilolite facies range within the range of unaltered glasses, except for one sample from the clinoptilolite facies (Fig. 15). One of four samples of the analcime-bearing facies from the Emirler deposit is situated within the range, but the others extend to higher SiO$_2$/(Al$_2$O$_3$ + Fe$_2$O$_3$) values. On the basis of this fact alone, it can be suggested that there is no change in the clinoptilolite facies with respect to silica but a gain in the analcime facies. However, there is a rough positive correlation between the (Na$_2$O + K$_2$O)/(Al$_2$O$_3$ + Fe$_2$O$_3$) and the SiO$_2$/(Al$_2$O$_3$ + Fe$_2$O$_3$) ratios of glasses and (glass + smectite) and analcime-bearing samples. The rhyolitic pumices of Cappadocian ignimbrites, erupted between 11 and 8 Ma in Central Anatolia, also plot on the same line and differ significantly in their SiO$_2$/(Al$_2$O$_3$ + Fe$_2$O$_3$) ratios even in the same unit (see Temel and Gündogdu in this issue). In addition, a loss of silica rather than a gain should normally be expected in this facies, because K-feldspar and analcime are low-silica minerals. Therefore, the supposed gain of SiO$_2$ in the analcime facies compared to the glasses, may be a result of the differences in original compositions of starting materials within the same unit.

A comparison for alkali and alkaline-earth elements shows significant loss of alkali from the glass, which is
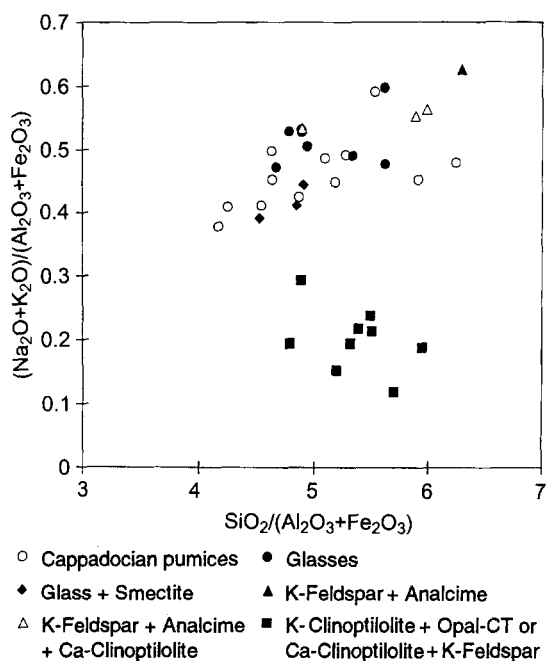

○ Cappadocian pumices   ● Glasses

♦ Glass + Smectite   ▲ K-Feldspar + Analcime

△ K-Feldspar + Analcime   ■ K-Clinoptilolite + Opal-CT or
+ Ca-Clinoptilolite   Ca-Clinoptilolite + K-Feldspar

Fig. 15. (Na$_2$O + K$_2$O)/(Al$_2$O$_3$ + Fe$_2$O$_3$) versus SiO$_2$/(Al$_2$O$_3$ + Fe$_2$O$_3$) in the glasses, zeolitized tuffs and pumices from Cappadocian ignimbrite (data from Temel and Gündogdu, this issue)

compensated by a gain of Ca and Mg from pore water (Fig. 16). Limited variations of Mg in clinoptilolites indicate that the alkali loss was essentially counterbalanced by Ca during the development of clinoptilolite-dominated facies. In the absence of whole-rock analyses, it is difficult to make an evaluation for the Degirmenli and Karaören tuffs, but the alkali and alkaline-earth contents, as well as the Si/(Al + Fe) ratios of their glasses and clinoptilolites (see Tables 1, 3), show that the same chemical changes took place during their transformation into clinoptilolite.
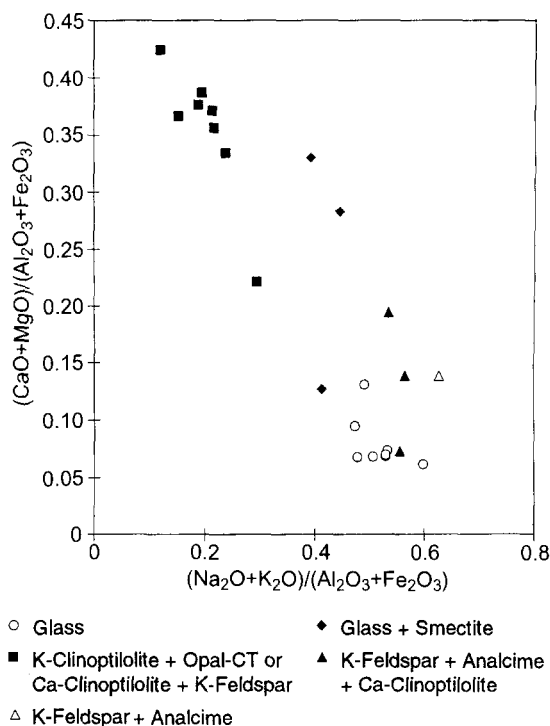
Fig. 16. Relations between $(CaO + MgO)/(Al_2O_3 + Fe_2O_3)$ and $(Na_2O + K_2O)/(Al_2O_3 + Fe_2O_3)$ ratios of samples representing different diagenetic facies in the Emirler and Köpenez deposits

Similar results have been found for silicic tuffs by other authors (e.g. Boles and Surdam 1979; Barrows 1980; Semelin 1985; Broxton et al. 1987; Sheppard 1991; Rice et al. 1992). The samples of glass + smectite ± calcite also exhibit a loss of alkalis, and consequently they lie between clinoptilolite and fresh glasses. The analcime-bearing samples have almost the same total alkali/ $(Al_2O_3 + Fe_2O_3)$ ratios, but high Na_2O/K_2O ratios compared to the glasses especially in the Emirler deposit. Some of them with smectite and/or calcite, give higher total alkaline-earth/$(Al_2O_3 + Fe_2O_3)$ ratios. The high Na_2O/K_2O ratios indicating a gain in Na and a loss in K, may be a consequence of starting materials or trapped pore waters relatively rich in Na and grain size of tuffs. The high $SiO_2/(Al_2O_3 + Fe_2O_3)$ ratios of analcime-bearing tuffs are not compatible with starting materials rich in Na because the Na_2O/K_2O ratio will be normally low in SiO_2-rich glasses due to plagioclase separation during magmatic differentiation. The alternation between coarse-grained analcime and medium to fine-grained non-analcime tuffs in the same section of the Köpenez and Emirler deposits, as noted already, diminishes the credibility of the Na-rich pore water hypothesis. Therefore, the grain size of tuffs seems to have been the most important factor during the development of the analcime facies, as will be discussed in the next section.

It can be concluded that silica content seems to be constant, and that the most important chemical changes which took place during the diagenetic transformation of volcanic glass to smectite and to clinoptilolite, are a loss in alkalis and a gain in alkaline-earths. The total of alkali

elements appears to have been preserved in the analcime-bearing facies.

Discussion

Formation of smectites

It has been noted by some authors (e.g. Sheppard and Gude 1968; Hay 1978; Barrows 1980) that the formation of dioctahedral smectites from volcanogenic material was favoured by a relatively low $(Na^+ + K^+)/H^+$ activity ratio of the solutions reacting with glass. However, the presence of dioctahedral smectites in all diagenetic facies indicates that they can form under different chemical conditions. Their formations and amounts should be controlled by Fe released during the dissolution of glass, because this element is easily incorporated into the smectite structure but not into that of other diagenetic minerals except the heulandite group which may contain it (see Table 6 and data in Barrows 1980; Moncure et al. 1981; Broxton et al. 1987; Lee 1988; Sheppard 1991; Münch and Cochemé 1993). Therefore, the low smectite content in the clinoptilolite facies is mainly due to the low Fe content of rhyolitic glasses and partly due to the incorporation of Fe into the clinoptilolite structure. Dioctahedral smectites of the investigated deposits show compositional variations, especially in their Fe content with regard to diagenetic assemblages. Montmorillonitic smectites with low octahedral Fe, are associated with glass, while beidellitic smectites rich in Fe are observed with zeolites or K-feldspar. This difference may indicate that the smectites associated with zeolites are the latest minerals as already concluded on the basis of SEM observations. More Fe will be released due to total dissolution of glass in the zeolite facies and a part of the aluminum must be moved from octahedra to tetrahedra by creating beidellitic smectite. A similar compositional difference was also noted in ferrierite-rich tuffs, where earlier smectites are rich in Mg, while the latest ones are rich in Fe (Rice et al. 1992). As for differences within montmorillonitic smectite associated with fresh glasses and within beidellitic smectites associated with K-feldspar, they seem to reflect the compositional variations in starting material as observed by Banfield et al. (1991).

Formation of zeolites and K-feldspar

The alternations between zeolitic tuffs and carbonate rocks (limestone and dolomite) which exist in all the basins, indicate that the pyroclastics were zeolitized in saline lacustrine environments rich in Ca and Mg ions. This is mainly due to the presence of lithologies such as carbonates and ophiolitic rocks in the areas that surround the basins. The formation of sedimentary magnesite deposits in some basins (Gündogdu and Ataman 1976) located in the vicinity of the Emet basin supports this opinion.

Experimental studies show that the most important chemical parameter controlling the Si/Al ratio of zeolites is the pH of the solutions (Mariner and Surdam 1970;

Barth–Wirsching and Höller 1989). Under experimental conditions where the pH of the reacting system is not too high, zeolites formed from silicic glass exhibit the same Si/Al ratio as the starting material and a further increase in pH leads to the formation of zeolites with a low Si/Al ratio (Barth–Wirsching and Höller 1989). The existence of carbonate minerals in all diagenetic facies except those rich in clinoptilolite, shows that the pH of pore water trapped during the deposition of the tuffs was probably higher than 8.5 (Garrels and Christ 1965). The similarity between clinoptilolites and rhyolitic glasses in terms of Si/(Al + Fe) ratio may indicate that the pore water pH was lower than 10 (Barth–Wirsching and Höller 1989). Therefore, it may be suggested that the diagenetic transformation of the tuffs occurred within a pH interval of 8.5 to 10. By taking into consideration geological and hydrological data, a similar pH interval (8.5 to 9.5) was also proposed by Surdam and Sheppard (1978) for zeolite formation from silicic glass. On the other hand, Boles and Surdam (1979) supposed that clinoptilolite formation occurred at a pH of less than 8.5 on account of the general absence of calcite and dolomite in the Ca-clinoptilolite diagenetic facies. However, the absence of carbonate minerals cannot be used in this way, because the formation of calcite or dolomite will be possible if Ca is not consumed by other earlier diagenetic minerals especially by clinoptilolites as concluded previously.

The development of clinoptilolite-dominated facies seems to be the result of differences in the salinity of the trapped pore water, and the grain or pore size and permeability of the tuffs, rather than the effect of initial pH of lake water or starting material, because the K- or Ca-clinoptilolites of all deposits have almost the same Si/(Al + Fe) ratio. It can be explained in the following manner. As already discussed, during the formation of clinoptilolite the alkaline-earth elements are removed from trapped pore water and alkalis are released from glass. After this reaction, the pore solutions will become highly alkaline and more basic in the pores or reacting systems where the solid or glass/liquid ratio is in inverse relation with pore size. In other words, the alkali/alkaline-earth ratio and the pH of pore solutions resulting from glass-clinoptilolite reaction will depend on the initial salinity of trapped lake water and the pore size. As a consequence, in lower salinity conditions where the initial pH is favourable for clinoptilolite formation, the quantity of alkali elements, especially that of K, will be relatively higher in clinoptilolite and lower in the pore solutions of very fine-grained tuffs where glass/liquid ratios are high. Because of the very low permeability of these tuffs, the low pH and K content of the pore solutions will be practically unchanged and not sufficient to form K-feldspar from glass. In this case, the K-rich clinoptilolite is associated with opal-CT due to the high residual silica content of the pore solutions. This interpretation is supported by the existence of opal-CT-like silica-rich granules with Al/K ratios higher than K-feldspar. In contrast, in the coarse-grained vitric tuffs where the glass/liquid ratio is relatively low in the pores, clinoptilolite will be rich in Ca and the pore solutions in K. The permeability will also enable the diffusion of K ions between the interconnected pores of these tuffs. Thus, the pH and K content of pore

solutions will increase before the complete transformation of glass to Ca-clinoptilolite, and make it possible to form K-feldspar from glass in the large pore spaces of ash tuffs as observed in Figs. 6a and 9c. At relatively higher salinities, the amount of K released from glass will be higher, and sufficient to form K-feldspar even in impermeable fine-grained tuffs. In the very coarse-grained tuffs deposited under the same conditions, analcime will also be formed as the latest mineral, in addition to Ca-clinoptilolite and K-feldspar. Because the pH and Na content of pore solutions increased continuously during the formation of Ca-clinoptilolite and K-feldspar, conditions necessary for the formation of analcime are reached before total consumption of the glass. These mechanisms of formation explain the vertical and lateral distributions of facies containing or dominated by K- and Ca-clinoptilolite in the Emirler, Köpenez and Karaören deposits, which are represented mainly by vitric tuffs. However, if the glass/fluid ratio of the whole system is low and the glass is relatively rich in alkaline-earth elements, as is the case in coarse-grained crystal tuffs, the differences in salinity, grain or pore-size, and permeability should not create the compositional variation in clinoptilolites that is observed in the Degirmenli deposits, where Ca-clinoptilolite is sometimes associated with calcite in the coarse- and fine-grained tuffs. Thus, the importance of grain-size and permeability as major factors in diagenetic alteration of volcanogenic material, as concluded by several authors (e.g. Hay 1966; Barrows 1980; Moncure et al. 1981; Gündogdu et al. 1989; Banfield et al. 1991; Lander and Hay 1993; Münch and Cochemé 1993), seems to be more important in vitric tuffs deposited in lower salinities. As for heulandites observed with K-feldspar in the Degirmenli and Karaören deposits, they were probably formed from starting material slightly different in the Si/Al ratio, because they alternate with Ca-clinoptilolites. Their relatively high Na contents compared to Ca-clinoptilolites may also indicate a starting material with a low Si/Al ratio. By taking into consideration their low Si/Al ratios, it may be suggested that the Karaören phillipsites were formed after K-feldspar.

The Si/Al ratios (about 3, 3) and the distribution of K-feldspars in the Degirmenli, Emirler and Köpenez deposits indicate that they were formed in more saline parts of paleolakes, where the initial pH of the lake water was relatively high during deposition of the tuffs, probably around 9.5 as indicated by experimental data (Barth-Wirsching and Höller 1989). Surdam and Sheppard (1978) considered that the K-feldspar has replaced other more silicic zeolite minerals (clinoptilolite, phillipsite), as well as analcime, in thin tuff levels deposited in saline, alkaline lake deposits. The replacement of silicic zeolites or smectites by analcime was also proposed by some authors (e.g. Surdam and Sheppard 1978; Hay 1966, 1978; Boles and Surdam 1979; Ratterdam and Surdam 1981; Taylor and Surdam 1981). These replacements, never documented by SEM observations, were based on the absence of silica-rich zeolites or analcime in K-feldspar-bearing tuffs, or on the high smectite content of analcime tuffs, and sometimes explained by hypothetical chemical reactions. However, the paragenetic relations of K-feldspar with glass and other authigenic minerals clearly show that, instead of

these replacement mechanisms, it was formed directly from the glass, but not from either clinoptilolite or analcime. This is also supported by the relationships between the Rb/Sr ratios and the Sr isotopic compositions of whole rocks and mineral fractions of the Köpenez deposits (Fig. 17). The initial $^{87}Sr/^{86}Sr$ ratios of glass (Fig. 17) are situated within the range (0.707 to 0.709) of andesitic to rhyolitic lavas in western Turkey that were contaminated by continental crust (Güleç 1991). The clinoptilolites and smectites probably represent the Sr isotopic ratios of paleolake water, because little difference was observed between these two minerals and calcite in the Bigadiç basin (see Gündogdu et al. 1989). This diagram thus represents a mixing line between the glass and paleolake water, and it indicates that clinoptilolite and smectite used not only Ca and Mg, but also Sr from pore water. It also shows that the Rb/Sr and initial Sr isotopic ratios of K-feldspar, whole rock and analcime fractions are close to those of glasses, and that these minerals were formed from glass. Therefore, under high pH conditions, after the formation of K-feldspar from glass, the pH will be relatively increased and then the released Na will react with glass to form analcime which has a lower Si/Al ratio (2.7) than K-feldspar. The intercalations of coarse-grained K-feldspar + analcime bearing vitric tuffs with the K-feldspar-bearing medium to fine-grained vitric or crystal tuffs in the Köpenez deposit, indicate that the petrographic type, grain size and permeability of the tuffs are also important parameters during the development of the K-feldspar + analcime facies, where quartz is a final product. The analcime may not occur due to limited Na diffusion in medium to fine-grained vitric tuffs or to high glass/liquid ratio in crystal tuffs. In some cases, K-feldspar formation may also take place even at the basin margin, where the initial pH of pore water is not sufficient for formation of clinoptilolite, as observed in smectite-rich and glass-bearing coarse-grained tuffs of the Karaören deposit. This may be explained by the relatively high K content of glass and the high permeability of the tuffs, as well as by the high rate of glass-smectite reaction. In other words, the concentration of K and the pH of pore solutions after glass-smectite reaction in coarse-grained tuffs, seems to have been favourable to the formation of K-feldspar from glass rather than clinoptilolite. This association was also obtained during the experimental alteration of rhyolitic glass with distilled water in an open system (Barth–Wirsching and Höller 1989).

Absence of silica-rich sodic zeolites

The silica-rich sodic zeolites (mordenite, erionite, chabazite and phillipsite) are absent in the clinoptilolite-dominated mineralogical parageneses of the investigated zeolite deposits which formed in saline lacustrine basins. In contrast, these minerals are commonly associated with clinoptilolite in some Cenozoic formations of the western United States (e.g. Lake Tecopa, Barstow, Big Sandy), which are considered as saline-alkaline lake deposits, particularly on account of the existence of trona and gaylussite in Lake Tecopa (Sheppard and Gude 1968, 1969, 1973; Surdam and Sheppard 1978; Hay 1978). Their scarcity, including that of trona, has also been put forward as an
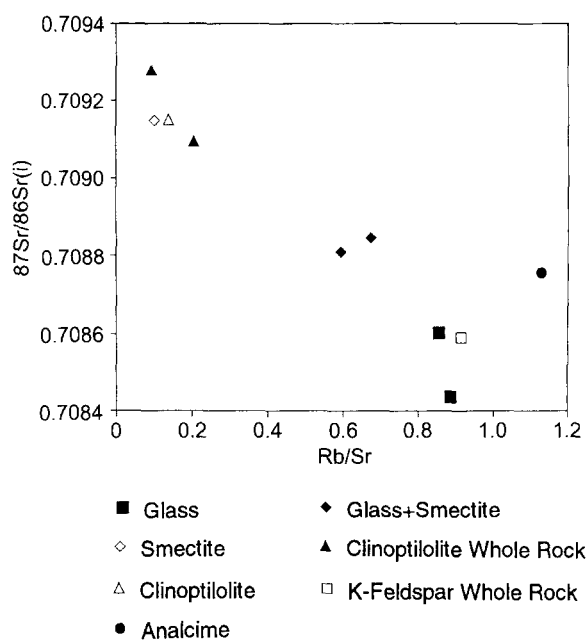

Fig. 17. Relations between 87Sr/86Sr and Rb/Sr ratios of separated minerals and whole rock of the Köpenez deposit (data from Claparols 1992, but the 87Sr/86Sr ratios were corrected to the stratigraphic age of the Köpenez deposit assumed to be 15 Ma)

argument to support non-alkaline conditions or low Na activities in lake water (Wagon Bed and Chalk Hills Formations; Boles and Surdam 1979; Sheppard 1991). However, the tuffaceous units of these formations are intercalated with carbonate rocks (limestone or dolomite), indicating saline depositional environments, as in the Bigadiç, Emet and Kirka basins. They also show a loss in alkaline elements as in the investigated deposits, because the silica-rich zeolite minerals or whole rocks contain more alkaline-earth elements than the glasses (see Sheppard and Gude 1968, 1969, 1973; Boles and Surdam 1979; Sheppard 1991). As previously noted, the glasses found in the USA zeolite occurrences, are richer in Na than those of the Bigadiç, Emet and Kirka zeolite deposits (see Table 1). Within the formations considered as saline-alkaline lake deposits, there are some contrasting relations between zeolite mineralogy and the presence of saline minerals. For example, analcime which is the most sodic zeolite, is a rare diagenetic mineral in the trona-bearing Lake Tecopa deposits (Sheppard and Gude 1968), as well as in the Beypazari trona deposit (Gündogdu et al. 1985), but it is very common in the Barstow formation where trona is absent (Sheppard and Gude 1969). These relations can only be explained by the high Na content of the Barstow glass compared to that of Lake Tecopa (see Table 1). In addition, the Cappadocian tuffs, also intercalated with limestone or dolomite and halite deposits, have similar zeolite mineralogy and K/Na ratios to Cenozoic tuffs of the western USA (see Temel and Gündogdu in this issue). Thus, these data indicate that the difference in zeolite mineralogy observed in saline lacustrine environments, is mainly due to the K/Na ratio of the starting material rather than the initial Na content of lake waters.

This interpretation is in accordance with experimental data demonstrating that the initial alkali content of dilute reacting solutions is of minor importance in the case of starting material rich in Na and K (Barth–Wirsching and Höller 1989).

Zeolite-borate relationship

As previously reported, the most important chemical changes which occurred during the diagenetic transformation of rhyolitic glasses to smectite or clinoptilolite, are losses of Na and K, particularly compensated by a gain of Ca from trapped pore water. The concentrations of the incompatible elements, such as B and Li, are high in K-rich volcanics which have been contaminated by crustal material (Morris et al. 1990; Leeman et al. 1994), such as the volcanics in western Turkey (Güleç 1991). These elements will also be enriched in pore solutions along with Na, K and Mg ions. During compaction of the pyroclastics, their pore solutions are added to lake water as brines and create a suitable environment for the formation of evaporitic minerals, e.g. the borates found along with Li-rich trioctahedral smectite and K-feldspar in the Bigadiç, Emet and Kirka basins, or trona associated with sepiolite, searlesite and K-feldspar as in the Lake Tecopa and Beypazari deposits, or halite deposits as in Cappadocia.

Conclusions

In the diagenetic evolution of silicic volcanic glass in a lacustrine environment, at lower salinities, where the pH is sufficient for total dissolution of glassy material, the first minerals will be silicic zeolites such as clinoptilolite. As a result of the increase in pH of the pore solutions, subsequent diagenetic minerals will be less siliceous. The identity of these minerals will depend on the K/Na ratio of the starting material, which is the major source of these elements. If it is too high, as in the investigated deposits, the subsequent diagenetic minerals will be opal-CT and K-feldspar + quartz, depending on the grain-size and permeability of the tuffs. The other zeolites such as mordenite, erionite, chabazite and also phillipsite in place of K-feldspar, which have nearly the same Si/Al ratio, will be formed if the K/Na ratio is low as in the case of Lake Tecopa, Barstow and Cappadocia. Analcime will also be formed as a later diagenetic mineral, depending on the Na content and grain-size of the starting material. In the central part of the basin, where the salinity and pH of lake water are highest, the K-feldspar + analcime diagenetic facies will occur and will be dominated by one of them depending on the K/Na ratio of glass and the grain size of the tuffs. The pore solutions, enriched in Na, K and Mg, as well as in B and Li after diagenetic transformation of silicic glasses, will be used in the formation of borates or trona associated with Mg-rich clay minerals and K-feldspar.

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