THE GENESIS OF A MORDENITE DEPOSIT BY HYDROTHERMAL ALTERATION OF PYROCLASTICS ON POLYEGOS ISLAND, GREECE

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Abstract—The vitric component of the silicic pyroclastic flows and surge deposits (Prassa ignimbrite unit), from the northwestern exposures of the pyroclastics formation of Polyegos Island, South Aegean Sea Volcanic Arc in Greece, is replaced by authigenic zeolite and clay minerals. Mordenite dominates, and clinoptilolite (heulandite type 3), illite and illite–smectite (I–S) are subordinate. Opal-CT, quartz, feldspar, biotite and halite complete the mineralogical suite. In the southwestern part of the pyroclastics formation (Myrsini pyroclastics unit), kaolinite, halloysite, alunite and amorphous silica are the major mineralogical constituents as a result of a strong hydrothermal alteration by solutions enriched in SO_4^{2-}. Scanning electron microscope (SEM) examination proved that the 1st type of zeolites formed within the area were heulandite minerals, following the formation of smectite, as a result of the activity of pore fluids within the volcaniclastic pile. There was no substantial evidence to support a hypothesis that mordenite was formed with the heulandite minerals after the initial stages of glass dissolution, other than some very minor mordenite that was formed from a gel-like type of material. The majority of mordenite present is most often draped over and formed from the crystals of heulandite minerals. Heulandite minerals often show advanced dissolution effects. The mineral dissolution was due to the emplacement of rhyolite lava domes and flows and the associated temperature rise and circulation of hydrothermal fluids, which had also mixed with seawater. The volcanic activity raised the temperature and changed the pore fluid chemistry, and the more unstable members of the heulandite minerals group were transformed to mordenite. Clinoptilolite (heulandite type 3), which was found within a few samples, was thermally more stable than any heulandite type 1 or 2 phases initially present. Therefore, clinoptilolite was either transformed more slowly or within a very few cases, it has not been affected at all. A heulandite-minerals-derived material acted as the major precursor for the formation of mordenite. The temperature increase within the area and the later hydrothermal alteration effect are also indicated by the illitization of the smectite. Mordenite is also found to have formed from I–S clays. Overall, mordenite formed as a result of elevated temperature and high Na^+ concentration.

Key Words—Clinoptilolite, Greece, Heulandite, Hydrothermal Alteration, Mordenite, Polyegos, Pyroclastics, Rhyolite, Zeolites.

INTRODUCTION

Mordenite, a high-silica zeolite mineral, is usually found with the heulandite minerals as an alteration product within volcaniclastic sequences. Generally, when zeolites were formed within saline and alkaline lakes, deep sea sediments and burial diagenetic environments by the hydration and dissolution of volcanic glass and the activity of pore fluids, the heulandite type of minerals was either the only phase recorded or it simply dominated the mineralogy, with mordenite less common (Sheppard and Gude 3rd 1973; Hay 1977; Moncure et al. 1981; Ratterman and Surdam 1981; Hay and Guldman 1987; Skarpelis et al. 1987; Tsolis–Katagas and Katagas 1989; Altaner and Grim 1990; Tsolis–Katagas and Katagas 1990; Tsirambides et al. 1993).

In contrast, mordenite commonly occurs within active geothermal areas as one of the earliest formed zeolites (Steiner 1955; Seki et al. 1969; Honda and

Muffler 1970; Kristmannsdottir and Tomasson 1978). There are some cases, in hydrothermal alteration settings, where mordenite was found to be the dominant zeolitic phase as an alteration product, within volcaniclastic sequences (Philips 1983; Sheppard et al. 1988; Pe–Piper and Tsolis–Katagas 1991). An example of active mordenite formation was given by Coombs et al. (1959) from Wairakei in New Zealand, where the mineral was being produced by the circulation of steam and hot solutions through rhyolitic tuffs and breccias.

Ellis (1960) produced mordenite from rhyolitic glass by placing it at a depth of 1045 ft in the Wairakei active geothermal area at temperatures of 230 °C and at pH 5.7. Recently, Wirsching (1976) formed mordenite from natural rhyolitic volcanic glass both in open and closed systems.

Seki (1973) provided a comprehensive literature review of experimental data regarding mordenite's conditions of formation. He concluded that mordenite can be synthesized from a variety of materials and conditions. Its thermal limit generally increases with increasing substitution of Ca for Na.

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Figure 1. South Aegean Sea Volcanic Arc (dashed line). Key: 1 = Korinthos area, 2 = Methana and Poros, 3 = Aegina, 4 = Milos, 5 = Kimolos, 6 = Polyegos, 7 = Santorini, 8 = Nisyros and Yali, 9 = Kos and 10 = Tilos.

In this study, we examine the genesis of a large mordenite deposit on Polyegos, Greece, formed under hydrothermal alteration conditions, in the vicinity of rhyolitic lava domes and flows.

GEOLOGICAL SETTING

South Aegean Sea Volcanic Arc

The samples came from the exposure of pyroclastic rocks on Polyegos Island, which belongs to the South Aegean Sea Volcanic Arc in Greece (Figure 1). The Arc (Paraskevopoulos 1958) starts from the volcanoes of the Korinthos area and extends to the east, including the islands of Methana and Poros, Aegina, the Milos group of islands with Milos, Kimolos and Polyegos, and Santorini. Its eastern boundary is the islands of

Nisyros, Yali, Kos and Tilos. The Arc is the result of the subduction of the African lithospheric plate under the Eurasiatic plate, which was initiated at the uppermost Miocene or early Pliocene (Mercier 1981; Jackson and Mckenzie 1988). The Arc became active during the Pliocene and remained so to the present time, reaching its maximum activity during the Quaternary (Mckenzie 1972).

Polyegos Island

Altogether, 53 samples were collected. They encompassed the entire outcrop of the Polyegos pyroclastics. These pyroclastics cover an area of 6 km² and their exposed thickness is about 200 m. The landform of the west-northwestern part is low and composed of
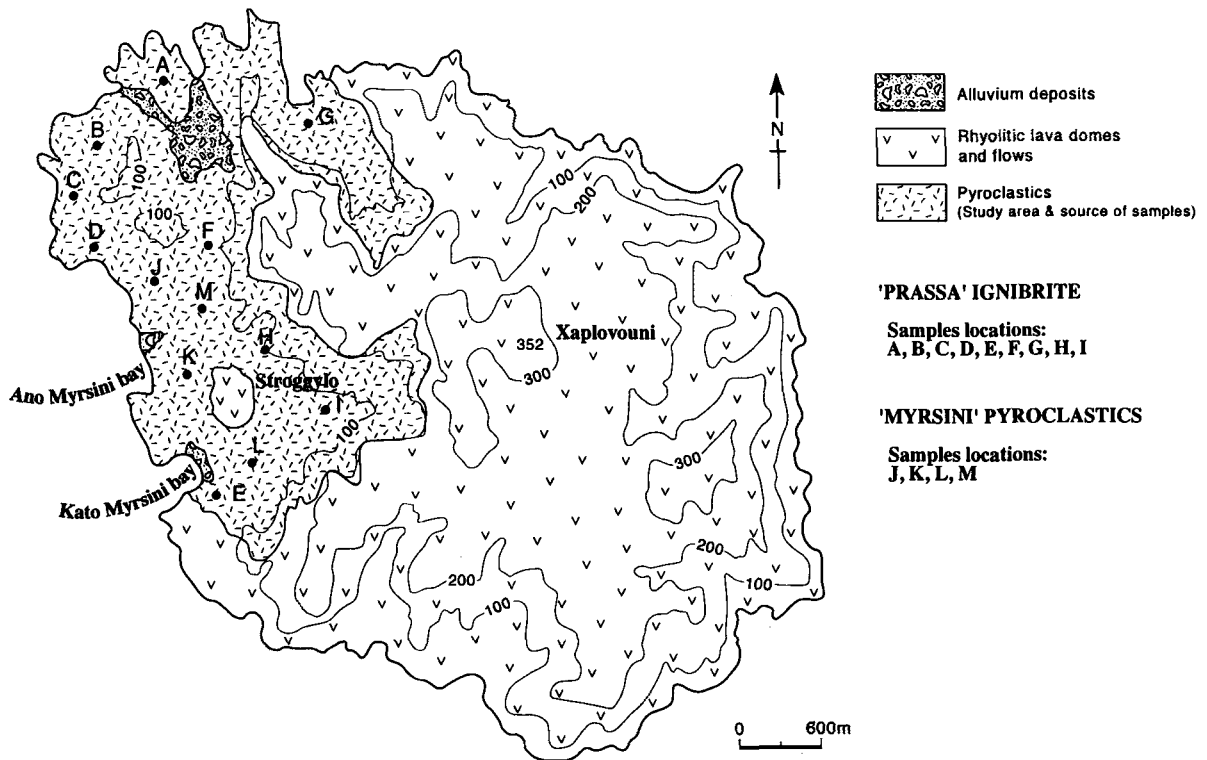
Figure 2.   Geological map of Polyegos island (Kanaris 1989).

hills up to 100 m in height. This part of the island is covered by the pyroclastic formation. The rest of the southern, northeastern and eastern parts is covered by lava domes and minor flows with a low absolute height of 352 m. The topography is extremely rugged because of the recent faults that affected the whole region of the South Aegean Sea Volcanic Arc.

Little was known of the geological structure of the island until recently. The geological map on which the sampling was based is part of a geological report by Kanaris (1989) of the Institute of Geological and Mineralogical Research of Greece (IGME) in Athens (Figure 2).

According to Kanaris (1989), the 1st volcanic products were tuffs which covered the west and the northwestern parts of the island (Figure 2). The northern exposures are green, but some parts from the southwestern area are white. They are tough, compacted and characterized by the lack of xenoliths. Following the deposition of the tuffs, rhyolitic lava domes and flows formed. Agglomerates formed around the main part of the domes. The lava eruptions were followed by the last events of the volcanic activity. Hydrothermal fluids circulated through the rhyolitic lavas and the tuffs, altering them and depositing Pb, Ba and Mn minerals in veins and flats. The hydrothermal fluids were also Si-rich, as evidenced from the silicification bands created within some areas (Kanaris 1989).

Although Kanaris (1989) considered the pyroclastics outcrop of Polyegos as a single unit of tuffs, formed from a single eruption, the pyroclastics were divided into 2 different units based upon lithological and depositional evidence (Fyticas and Vougioukalakis 1992). The 2 units were related to 2 entirely different eruption periods, an earlier one between 2 and 1.7 Ma and a more recent one between 1.1 and 0.9 Ma (Fyticas and Vougioukalakis 1992). The rhyolitic lava domes and flows in the eastern part of the island and around the area of Xaplovouni, and the small rhyolitic dome of Stroggylo (Figure 2), which according to Kanaris (1989) were the expression of the same volcanic activity, were also related to 2 different eruption periods.

During the 1st eruption period (2–1.7 Ma), which was the most intense and widespread volcanic activity in the area, the 1st pyroclastics unit, named the Prassa ignimbrite unit, was deposited on both the islands of Polyegos and Kimolos. In Polyegos, the Prassa ignimbrite was mainly deposited around the northwestern part of the island. In Kimolos, the unit was deposited around the eastern and northeastern parts of the island. The intrusion of the rhyolitic lava domes and minor flows (1.8–1.7 Ma), situated in the eastern part of the Polyegos island around Xaplovouni, concluded the deposition of this 1st pyroclastics unit (Fyticas and Vougioukalakis 1992).

Fyticas and Vougioukalakis (1992) stated that Prassa ignimbrite consists of submarine and terrestrial pyroclastic flows and surge deposits, and itself is subdivided into 2 parts. The lower part includes the pyroclastic flows, with a very finely crystallized ground mass of glass shards and pumice fragments, all of which have undergone extensive hydrothermal alteration. There is no clear evidence of sorting, but lapillito block-size fragments are mainly found in the lower horizons. The upper part includes a fine-grained, more massive tuff consisting of pumice fragments and glass shards again. Cross-bedding structures observed in places are indicative of surge depositional mechanisms. The Prassa ignimbrite unit was the precursor for the formation of the heulandite, mordenite, illite and I–S described in this paper.

During the 2nd period (1.1–0.9 Ma) a 2nd pyroclastics unit was deposited around Ano and Kato Myrsini bays. The unit was subsequently named the Myrsini pyroclastics. This eruption was less intense than the 1st and characterized by small-scale, local activity. The small rhyolite lava dome in the Stroggylo area is related to this eruption period (Fyticas and Vougioukalakis 1992).

The Myrsini pyroclastics consist mainly of pumice and some lapilli fragments of the Prassa unit. Glass shards are absent. They can be characterized as lapilli tuffs that, like the older Prassa unit, have undergone hydrothermal alteration. The type of alteration around this area can be described as an intensive hydrolytic, acid sulfate alteration. This is evidenced from the presence of alunite–kaolinite/halloysite–quartz assemblages and Fe-rich bands in the area (Hemley and Jones 1964; Hemley et al. 1969; Rye et al. 1992; Kitsopoulos 1995).

The sample locations are illustrated in Figure 2 in order to give an idea of the extent of each of the pyroclastics units on the island. Samples from locations A through I come from the Prassa ignimbrite unit; samples from locations J through M come from the Myrsini pyroclastics unit. Although the mineralogy of the Myrsini pyroclastics samples was also investigated, this study focuses on samples from the Prassa ignimbrite, where abundant mordenite is found.

ANALYTICAL METHODS

The mineralogy of the Prassa ignimbrite samples was examined by means of X-ray diffraction (XRD) and SEM; that of the Myrsini pyroclastics, only by XRD.

For the XRD analysis, micronized powders were packed into Al-holders and scanned from 2 to 65° at a speed of 1°/min using CuKα radiation from a Philips PW 1729 diffractometer. Clay mineralogy was identified from the <2-μm clay fraction. Air-dried, glycolated and heated oriented mounts were prepared from each sample.

Broken surfaces and polished thin sections of selected samples were examined with a Hitachi S520 SEM operated at 20 kV and linked to a LINK AN1000 energy dispersive spectrometer.

RESULTS AND DISCUSSION

Mineralogy

The alteration of the Prassa ignimbrite pyroclastics from Polyegos Island resulted in a series of authigenic minerals including zeolites and clays. Mordenite dominates the authigenic mineralogy and forms brown-colored, rounded fiber-like masses. Estimates from thin sections and SEM suggest that the percentage of mordenite in the samples can range from 40 to 90%, with the majority of the samples composed of 60–70% mordenite.

The SEM examination confirmed the XRD results that the Prassa ignimbrite samples from the northern Polyegos are dominated by mordenite, and revealed the morphological types of mordenite (Figure 3).

Mordenite forms "intertwined masses" (Figure 3A) and "intertwined bundles" (Figure 3B). The latter formed from a nucleus. Intertwined, partly spherical features whose internal part is an amorphous gel precursor and whose external consists of spindly fibers of mordenite were also identified (Figure 3C). Other morphological types of mordenite occurrences include a "fan" form (Figure 3D), a "filiform" type (Figure 3E), a "crisscrossing" form (Figure 3F), a "spider-web" shape bridging the space between other phases (Figure 3G) and a "rat-nest" feature (Figure 3H).

Heulandite minerals were found in only 8 samples out of 53. In order to classify them, the thermal tests as proposed by Alietti (1972) and Boles (1972) were followed. The reduction of the intensity of the 020 diffraction peak after heating at 560 °C for 12 h ranged from 0 to 6%, with only 1 sample showing a reduction of 18%. Following the suggestions made by Alietti (1972), Boles (1972) and Boles and Surdam (1979), the heulandite minerals found were all classified as heulandite type 3, clinoptilolites.

The clay minerals present were mainly illite and I–S. Opal-CT was also identified in the samples, based on its XRD pattern and its spherulitic feature of closely packed crystals (Figure 4). Mordenite clearly postdated opal-CT. Pyrogenic phenocrysts of feldspars, quartz and traces of biotite were also found. The presence of halite indicated the involvement of seawater during the alteration procedure.

The mineralogical pattern of the Myrsini pyroclastics was completely different from that of the older Prassa ignimbrite unit. The Myrsini materials were mainly white in color. Kaolinite, which is found in traces in only a few of the Prassa ignimbrite samples, was the dominant component within the Myrsini pyroclastics in the forms of both kaolinite and halloysite.
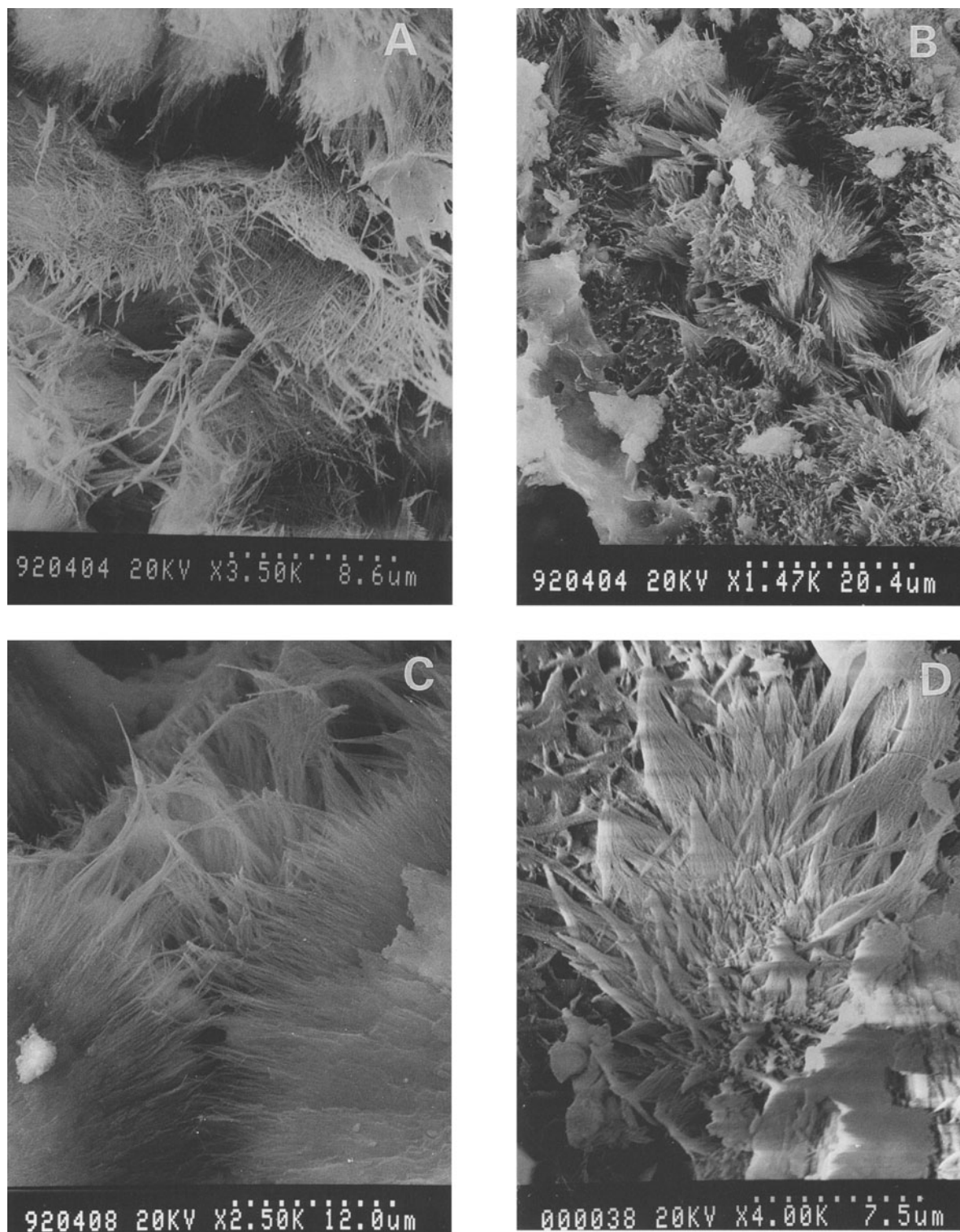
Figure 3.   A) Intertwined masses of mordenite. B) Intertwined bundles of radiating mordenite that have formed from a nucleus. C) Intertwined, partly spherical, features whose internal part is an amorphous gel precursor and whose external part consists of spindly fibers of mordenite. D) Fan-type mordenite where braids of diverging thread-like mordenite can be seen. (Mordenite in B and D has been formed on I S flakes. Mordenite in C has been developed from a gel type of material.) E) Filiform mordenite. F) Crisscrossing mordenite. The cubic crystal shown is halite. G)"Spider-web" type of mordenite formed by a tangle of curved filiform mordenite. H) "Rat-nest" mordenite.
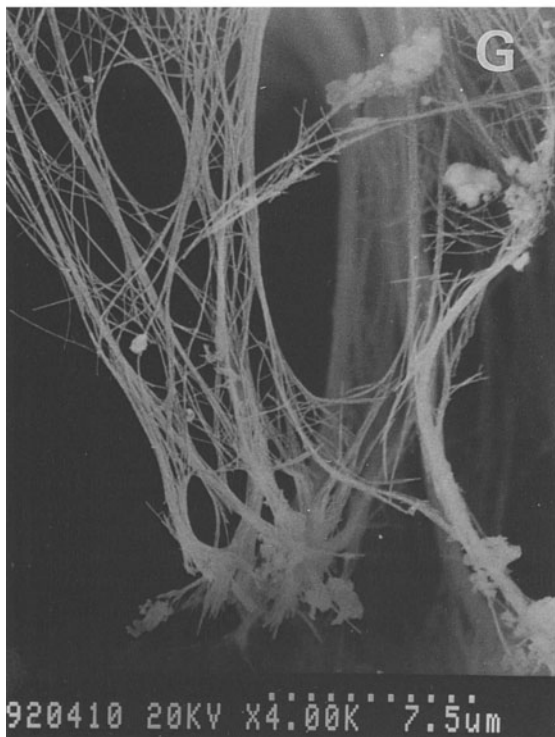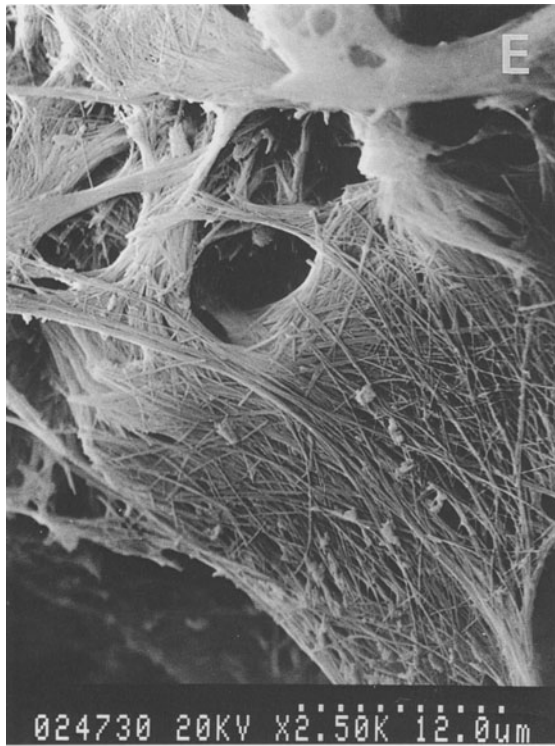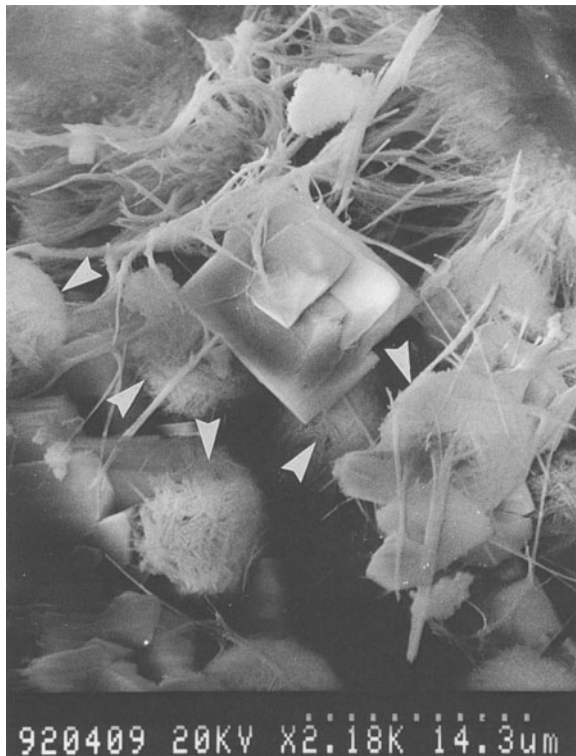
Figure 3.   Continued.

Figure 4. Lepispheres composed by closely packed bladed authigenic opal-CT crystals (shown by the arrows). Note that mordenite fibers postdate both opal-CT and the crystals of heulandite minerals. The latter have already started to dissolve (lower left corner). The crystal in the middle should be a form of dissolved crystal of a heulandite mineral upon which mordenite starts to develop.

Opal-CT, quartz and amorphous silica completed the mineralogical composition. For some of the samples, the alteration had progressed further to include alunite as the dominant phase with only a minor kaolinite and/or halloysite component.

Genesis of mordenite

A PROPOSED MODEL. The deposition of the Prassa ignimbrite (2–1.7 Ma) in the area was followed by the initial formation of smectite. Smectite was formed by hydrolysis of the volcanic glass in the presence of pore fluids. Interstitial water and/or meteoric water played the role of the pore fluids at this stage. The hydrolysis involved cation exchange between the solid phase (volcanic glass) and the pore fluid, which usually leads to the dissolution of the volcanic glass. Smectite is typically the first mineral to form at the expense of glass at a relatively low level of $(Na^+ + K^+)/H^+$ activity ratio of the pore fluid (Hemley 1962). As a result of the release of hydroxyl ions into the fluid phase from the formation of smectite, an increase of pH and the a_{SiO2} and enrichment of the pore fluid with respect to Na^+, K^+ and Si, leads to the formation of the heu-

landite type of zeolites (Hay 1966; Hay and Sheppard 1977; Hay and Guldman 1987).

During the hydrothermal alteration event that followed, the main precursor for the formation of mordenite was the pre-existing heulandite type of minerals. Other phases that acted as a minor precursor for the formation of mordenite were the authigenic clay phases and a gel-like type of material.

THE INITIAL AUTHIGENIC MINERALOGY. Markopoulos and Christidis (1989) observed that the Prassa ignimbrite from the Kimolos area has been chiefly altered to smectite. Opal-CT, quartz, clinoptilolite, mordenite and K-feldspar complete the mineralogical suite. They also concluded that "a hydrothermal system supplied with sea water, altered the original vitric tuffs and lavas, to bentonite with zeolites and authigenic K-feldspar, kaoline and alunite according to the pH of the acting solution".

The examination of the part of Prassa ignimbrite exposed at Polyegos indicated that the igneous protolith was acidic, probably a dacite–rhyodacite type of rock (Kitsopoulos 1995). The formation of smectite from an acidic protolith requires the removal of the excess Si and alkalis present in the protolith. Because of this fact, the existence of a semi-open system in the northeastern part of Kimolos is postulated. This type of system would have facilitated the removal of part of the excess Si and alkalis from the igneous acidic protolith and resulted in the formation of extensive smectite deposits. However, the presence of opal-CT and zeolite minerals within the smectite zone in Prassa (Markopoulos and Christidis 1988) indicates that sufficient Si and alkalis were retained to allow the formation of these phases; hence, the inference of a semi-open system. It is obvious that, if the system were fully open, all Si and alkalis would have been removed, and smectite would be the only phase present.

In contrast, the dominant phase from Polyegos was zeolite minerals rather than smectite. In addition, no lateral or vertical mineralogical zonation was observed throughout the area. This implies that the zeolitization took place at constant conditions. On Polyegos, it seems that exactly the same glass alteration procedure (hydrolysis) took place, involving the initial formation of smectite, but the important difference here was that the system was apparently rather closed. The excess Si and the alkalis, which were released into the pore fluid during the formation of smectite, were not removed. They remained within the system and resulted in the formation of the 1st zeolite minerals. Under these conditions, clinoptilolite (heulandite 3), and possibly some heulandite type 1 and/or 2, were formed. The pH of the fluids might have ranged between 7 and 9 in order for the siliceous zeolite clinoptilolite to form (Mariner and Surdam 1970; Sheppard et al. 1988). The formation of a K-rich mineral, such as clinoptilolite,
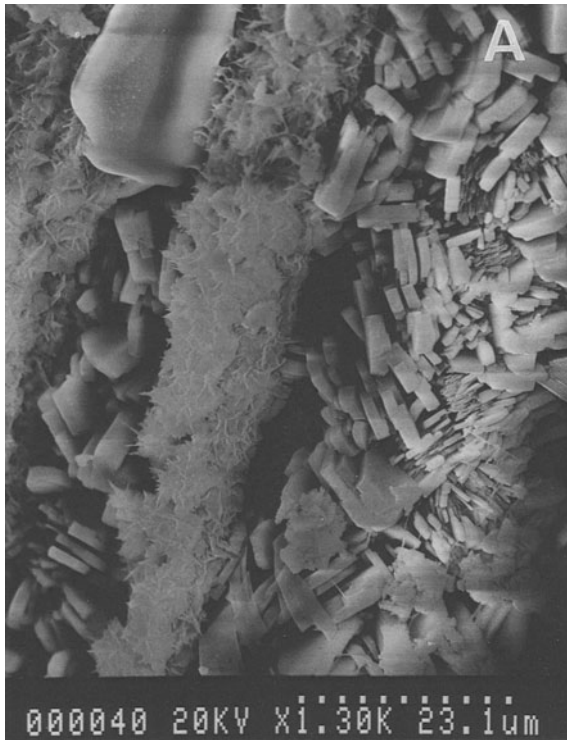
should have left the pore fluid Na$^+$-rich. A rise in temperature might have favored the formation of some mordenite. Any excess silica would form opal-CT. For Polyegos, illite and I–S were recorded as the dominant clay minerals rather than pure smectite. The existence of smectite or I–S has been reported by Sheppard et al. (1988) from the deeper clinoptilolite–mordenite authigenic zones from Yucca Mountain in Nye County, Nevada. It is likely that for Polyegos the 1st authigenic phase was actually a simple smectite phase, as it was for Kimolos. The smectite was later affected by illitization under rising temperature conditions and the hydrothermal alteration event that followed.

HYDROTHERMAL ALTERATION. The intrusion of the rhyolitic lava domes at Polyegos (1.8–1.7 Ma) in the proximity of the zeolite zone, which followed, caused a further increase in the temperature of the materials and the subsequent circulation of hydrothermal solutions. Kanaris (1989) accepted that the intrusion of the rhyolitic bodies was quite violent as indicated by the formation of the agglomerates around the lava domes. The area was also affected by intense tectonic activity and faulting. Hydrothermal fluids, associated with the rhyolitic bodies, circulated through the faults. The same fault system should have facilitated the gradual introduction of seawater and mixing with the hydrothermal solutions. Kanaris (1989) stated that the hydrothermal fluids affected the pyroclastics, the rhyolitic lava domes and the agglomerates. The ultimate result of the combined volcanic and tectonic activity was the creation of a more open system in the area and a change of the pore fluid chemistry.

Intrusion temperatures for rhyolite lava and pumice can range from 735 to 925 °C (Carmichael et al. 1974), which would result in radical changes in the mineralogical composition. The crystal structure of heulandite type 1 and 2 minerals is not as stable as type 3 heulandite (clinoptilolite). Therefore, any types 1 and 2 present were probably the 1st to be destroyed. Heulandite type 1 and 2 minerals are usually the Na- and Ca-rich members of the group. This might have resulted in the release of Na and Ca and the formation of a precursor that favored the formation of mordenite. The extensive hydrothermal alteration of the samples does not allow us to prove unambiguously that heulandite types 1 and 2 were present. With the exception of the samples where crystals of clinoptilolite (heulandite 3) were perfectly preserved, they were positively picked up by XRD, and

Figure 5.   A and B) Successions of glass shards initially altered to smectite, now an I–S material, and bands of heulandite mineral crystals can be identified. In this sample, the heulandite minerals are not etched or dissolved; therefore, it

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was possible for them to be positively identified by XRD, and they were classified as clinoptilolites using thermal tests. The latter were formed in the space between the glass shards following glass dissolution. The smectite in 5A suffered greater illitization than the smectite in 5B.

thermal tests could be applied to them, in the rest of the samples, the heulandite mineral crystals were severely etched and dissolved, and/or mordenite had already started to develop on them. Therefore, there were no heulandite type 1 and 2 crystals found intact to allow us to obtain complete, meaningful and correct microanalyses. However, remnants of heulandite minerals were extensively recognized, using SEM, as a major precursor (discussed in the next section; Figures 7B, 7C and 7D) from which mordenite was formed. Qualitative spectra obtained from some remnants of the heulandite minerals clearly indicated the strong presence of Na and Ca. In contrast, K was found in minimal amounts only. If clinoptilolite (heulandite 3) was the only heulandite mineral phase initially formed, then the spectra of the remnants of the heulandite minerals found today should indicate greater amounts of K than Na or Ca. In addition, we should note that the majority of the Polyegos samples are dominated by mordenite with a typical crystal chemistry (Na- and/or Ca-rich mordenites) that resembles this of the heulandite type 1 and 2. Excessive Na, which was needed to form the Na-rich mordenites, was probably introduced by the mixing of seawater with the hydrothermal fluids (discussed in the following paragraphs). However, the analyses of thermal spring water from Kimolos did not show any particularly high amounts of Ca. In addition, there was no evidence found to indicate an influx of Ca into the system. Therefore, it seems that most of the Ca that formed the mordenites was initially present. All of these facts are strong indications that heulandite type 1 and 2 minerals might have been present.

It is known that Na is usually found in greater amounts within mordenite's structure than heulandite's. The mixing of the hydrothermal fluids with the seawater would have provided the Na$^+$ that was required for the formation of mordenite. The presence of clinoptilolite, which in this case is K-rich and stable at temperatures up to 760 °C, within the same samples, indicates that such crystals were either transformed more slowly, or not affected at all, although the stability field even of clinoptilolite eventually decreases with increasing temperature (Bowers and Burns 1990). On Polyegos, the degree of the transformation and the dissolution of the clinoptilolite crystals was probably dependent on temperature. It is important to note that intact clinoptilolite crystals were only found within samples collected at maximum distances from the rhyolitic intrusions.

Heulandite Minerals as a Precursor for the Formation of Mordenite-SEM Evidence

The SEM examination of the few samples where clinoptilolite (heulandite 3) was present and was positively identified by XRD and thermal tests confirmed that the initial authigenic mineralogy was dominated
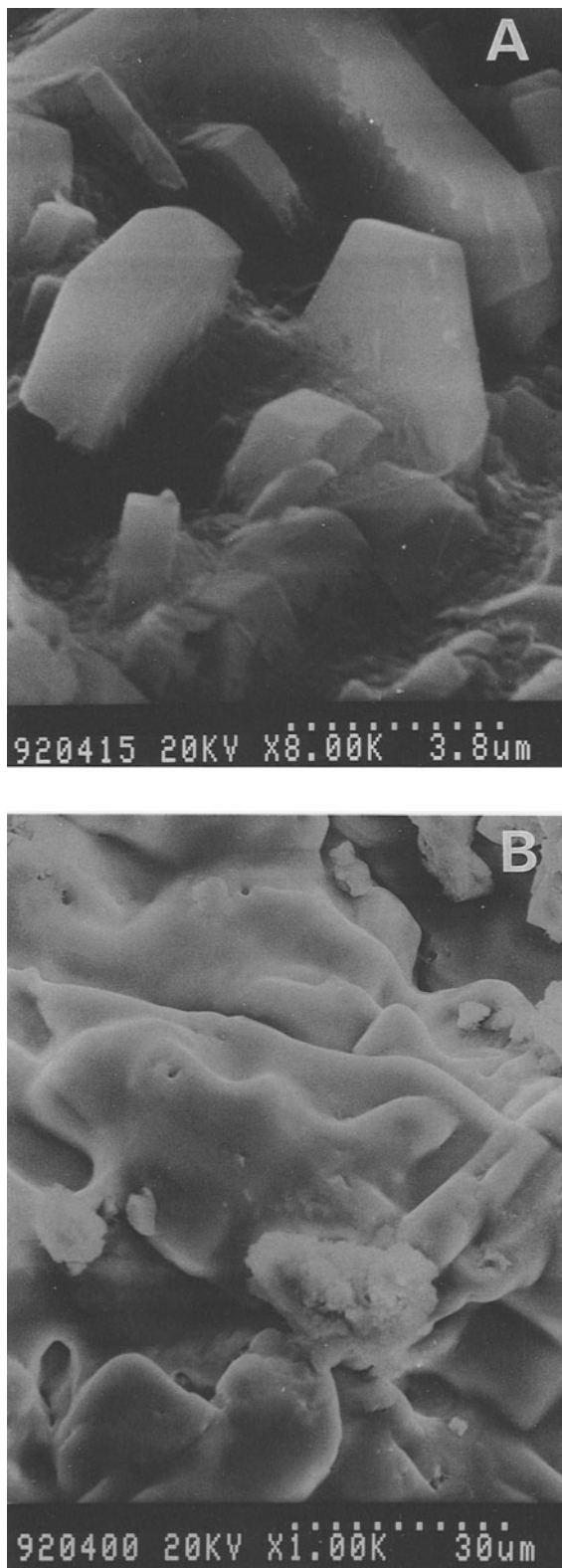
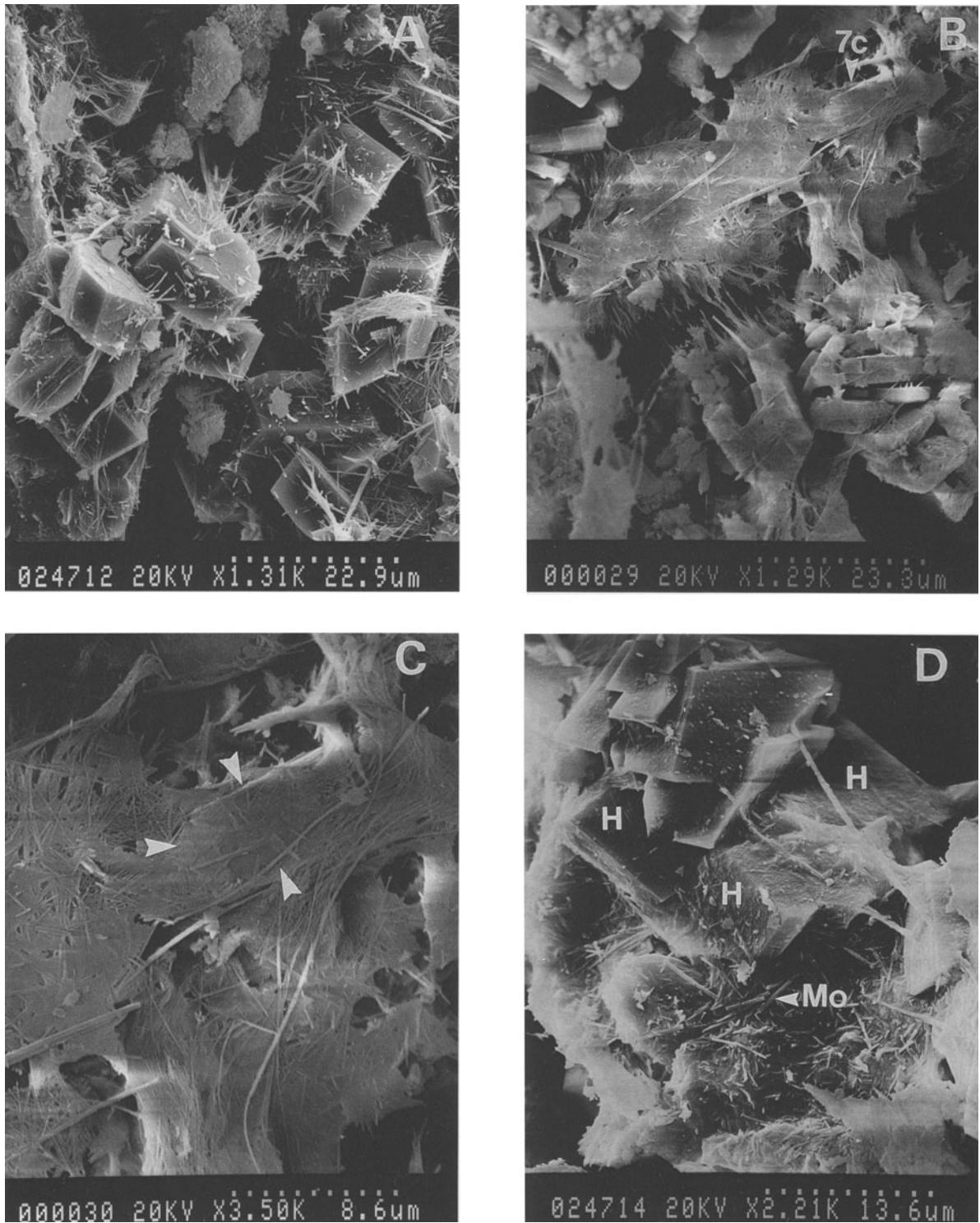Figure 6.   A and B) Dissolution effects on heulandite mineral crystals.

Figure 7.   A and B) Mordenite fibers draped along crystals of heulandite minerals. In the upper part of B, the alteration has progressed further and mordenite has completely replaced the heulandite minerals. C) A close-up view of the area marked as "7c" in B. Mordenite has completely replaced heulandite minerals. The arrows show what could initially be a crystal of heulandite minerals. D) The dissolution of crystals of heulandite minerals had already developed an amorphous precursor upon which mordenite needles started forming. H = heulandite type of minerals, Mo = mordenite.
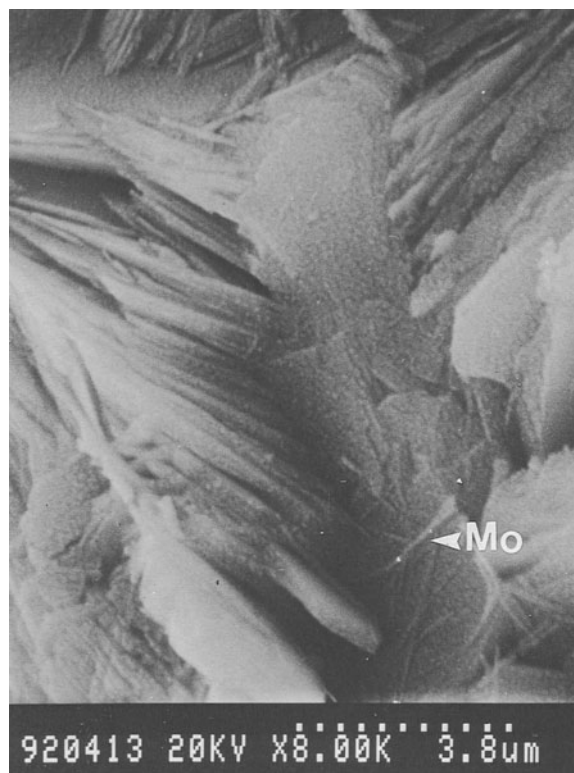
Figure 8. Laths of heulandite minerals that had undergone dissolution. Mordenite can be seen, in the area shown by the arrow, starting to develop on the laths' surface. Mo = mordenite.

by smectite and heulandite minerals in general (Figures 5A and 5B). Successions of glass shards altered to clays, and bands of clinoptilolite crystals can be identified. The clinoptilolites were formed between the glass shards following glass dissolution. It is obvious from Figure 5A that the initially formed smectite must have already suffered some degree of illitization as shown by the more platy flakes. In Figure 5B, the clay minerals are I–S, and they are inferred to have a greater expandability than the clays in Figure 5A, based on morphology. Keller et al. (1986) showed that, for the I–S series, the morphology can change from the "honeycomb", "corn-flake" or "maple leaf" types of smectite to the typical platy or scalloped with curled points types of illite.

For most cases, though, heulandite minerals showed dissolution effects, presumably being the precursor for mordenite formation (Figures 6A and 6B).

Mordenite was mainly found draped along heulandite mineral crystals, and it seems to have formed at the expense of these crystals (Figures 7A through 7D). It is clear, wherever the alteration process had progressed, that only remnants of heulandite minerals were identified to form a precursor over which mordenite was formed (Figures 7C and 7D). Laths of heu-

landite minerals can also be seen in Figure 8 starting to dissolve, and mordenite fibers can be observed developing on their surface.

It is obvious that the heulandite minerals shown in Figures 6, 7 and 8, unlike Figure 5, have been etched and/or have suffered by dissolution during the hydrothermal alteration. The fact does not allow the safe classification of these heulandite phases as heulandite 1, 2 or heulandite 3 (clinoptilolite).

The examination of polished thin sections, in addition to the broken surfaces, confirms the proposed genetic relationship. Mordenite was formed at the expense of heulandite minerals, along the welded glass shards (Figures 9A and 9B), where mordenite masses have taken the place of heulandite minerals within the matrix (Figure 10). The texture of Figure 9 (almost parallel bands of material) resembles the formation of clinoptilolite (heulandite 3) between glass shards following glass dissolution (as shown in Figure 5). However, in this sample heulandite minerals cannot be classified as heulandite 1, 2 or clinoptilolite (heulandite 3) because they were not picked up by XRD and, therefore, thermal tests could not be applied. In this case (Figures 9A and 9B), the majority of the lighter-gray area between the shards was identified as mordenite. Some remnants only of heulandite mineral crystals can be sporadically identified towards the central parts of the shards. It is obvious that, in this case, the hydrothermal alteration has gone further. In addition, Figure 9 provides the evidence for the circulation of the hydrothermal fluids through the pyroclastics because the very bright areas were identified as barite crystals.

Nothing indicates a radical change in the genetic conditions that would halve the initial formation of heulandite minerals. Therefore, based on Figures 5 to 9, we conclude that the initial authigenic zeolite minerals were, in general, heulandite minerals, and that a heulandite-minerals-derived material acted as the major precursor for the formation of the Polyegos mordenite.

The Relationship of Heulandite Minerals with Mordenite under Hydrothermal Conditions: The Role of Temperature, pH and Na^+ Concentration

It is known that mordenite is favored over heulandite minerals at higher temperatures and that there is a relationship between temperature and the occurrence of clinoptilolite and mordenite (Wirsching 1976; Hawkins et al. 1978; Philips 1983; Bargar and Beeson 1984). Filiform mordenite has been reported to grow on clinoptilolite from Miocene silicic tuffs at Yucca Mountain, Nye County, Nevada. Its formation was attributed to diagenetic reactions from a relatively high-temperature thermal regime (Sheppard et al. 1988). Surdam (1985) believed that the distribution of clinoptilolite and mordenite from the Miocene Obispo Formation of California was related to their proximity
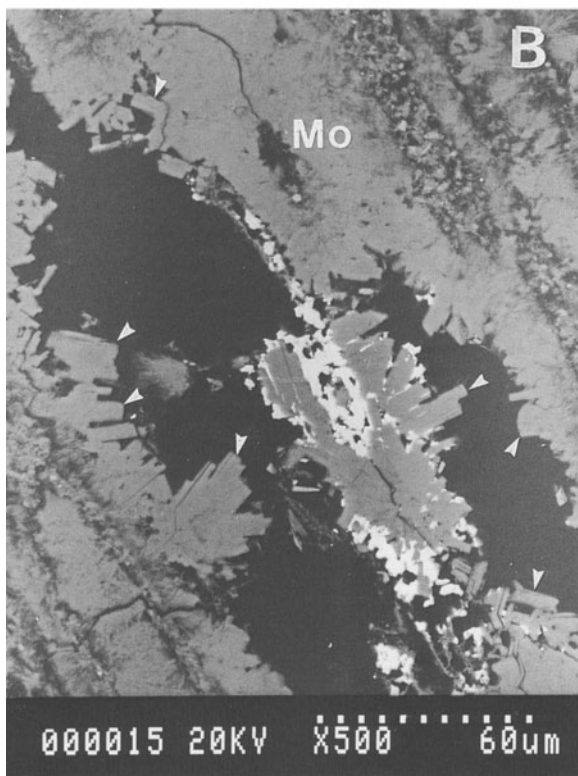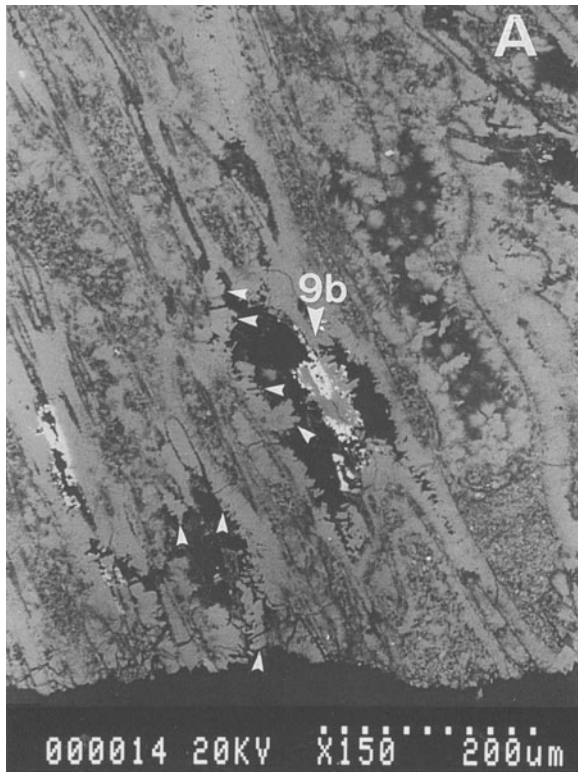
Figure 10.   Mordenite is formed at the expense of heulandite minerals in the tuff's matrix.

to intrusive bodies. Bish et al. (1982) found that, for the clinoptilolite-rich tuff from the Yucca Mountain, mordenite was formed from clinoptilolite after lengthy hydrothermal exposure at 120 and 180 °C. During hydrothermal experiments, mordenite, analcime and albite were synthesized from natural clinoptilolite at temperatures from 120 to 400 °C and at pressures from 50 to 650 bars (Kusakabe et al. 1981). Three factors control which of the minerals will form: temperature, pH and Na^+ ion concentration. It was shown that mordenite was formed from clinoptilolite at higher pH and Na^+ concentrations. During the same hydrothermal experiments (Kusakabe et al. 1981), the formation of analcime was restricted to conditions of pH not less than 12 as well as Na^+ concentration over 10,000 ppm. Temperature boundaries between clinoptilolite and mordenite, mordenite and albite, mordenite and analcime, and analcime and albite shifted to lower temperature when either pH or Na^+ increased. Thermal spring (46–56 °C on the surface) water from Kimolos Na^+ concentration ranged from about 10,500 to 11,500

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Figure 9.   A) Masses of mordenite taking the place of heulandite minerals along glass shards. The bright white crystals have been identified as barite. The small arrows show remnants of heulandite minerals. B) A close-up view of the area marked as "9b" in A. The crystals shown by the arrows are heulandite minerals. Mo = mordenite.
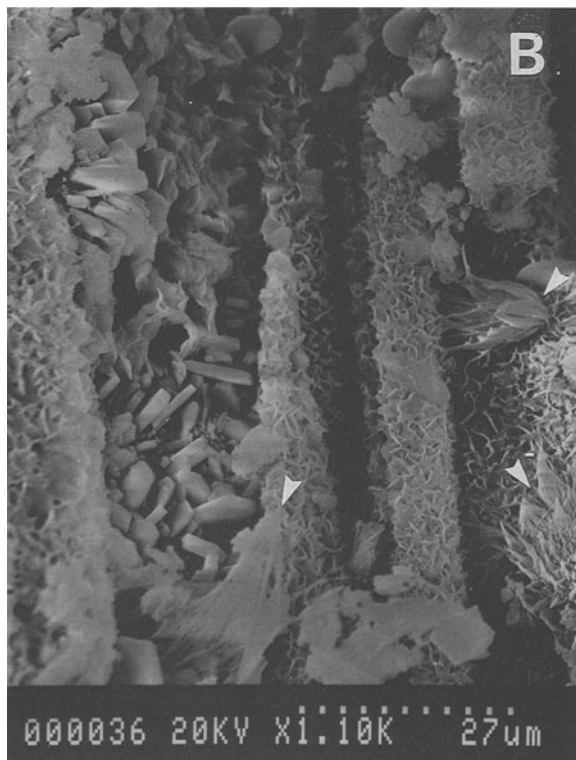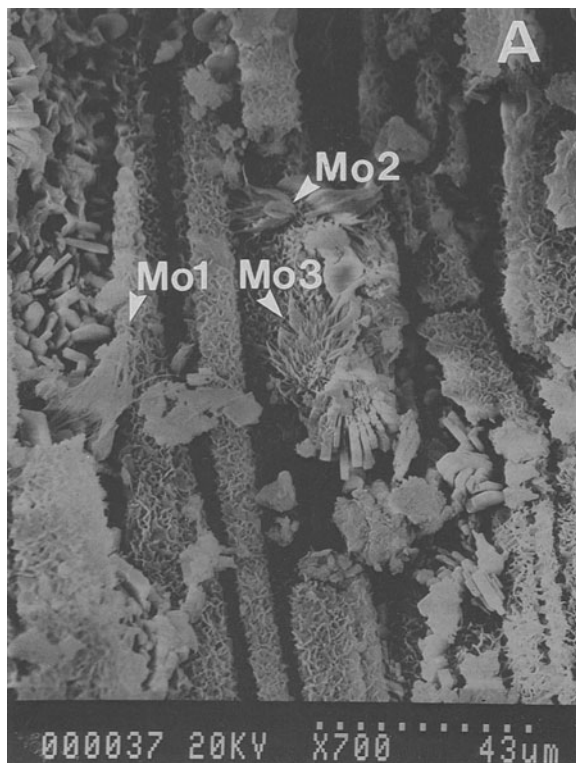
Figure 11.   A) Mordenite bundles (Mo1 and Mo2) and fan-type mordenite (Mo3) are developed from smectite/illite–smectite flakes. B) A close-up view of the same mordenites

ppm, very close to the Na$^+$ concentration (12,000 ppm) of seawater (Fyticas and Vougioukalakis 1992). If we accept that the hydrothermal fluids have a Na$^+$ concentration similar to these springs, according to the experimental work of Kusakabe et al. (1981), and since neither authigenic analcime nor albite was found within the area studied, we conclude that high temperature and high Na concentration should have favored the formation of Polyegos mordenite, but that they were not high enough to form analcime and/or albite. We can also conclude that the pH of the system did not exceed 12.

Other Phases as a Precursor for the Formation of Mordenite

An additional phase that may have also acted as a precursor for the formation of mordenite was some early-formed I–S, formed under an increasing temperature regime (Figures 11A, 11B and 12). The 2 intertwined bundles of radiating mordenite (Mo1 and Mo2 in Figures 11A and 11B) and the fan-type mordenite (Mo3 in Figures 11A and 11B) developed from what appears as I–S flakes. Note that Mo1 formed over the crystals of heulandite minerals. This indicates that its formation definitely postdated heulandite minerals. The mordenite shown in Figures 3B and 3D (Figure 3D is an enlargement of Mo3) also developed from the I–S flakes. Pe–Piper and Tsolis–Katagas (1991) and Sheppard (1994) have reported the formation of mordenite from authigenic smectite phases.

Some very minor mordenite has developed from a gel-like material that probably was derived from the glass alteration. The material has an amorphous morphology and it does not resemble any of the known crystal phases. Therefore, it is difficult to obtain its exact composition by microanalysis, and to distinguish the degree of alteration of this gel-like material. Qualitative analysis indicated the presence of Si, Al, Ca and minor amounts of Fe, Na and K. The mordenite shown in Figure 13 has developed from this gel-like material. A possible explanation for the existence of this gel-like type of material can be found from the initial stage of the alteration. The alteration of glass, under cation exchange procedures between a solid phase and the pore fluid, does not necessarily lead to glass dissolution and a gel phase (leached-layers glass) often persists (Shiraki and Iiyama 1990). A similar phase may have formed initially to act as a precursor for the formation of smectite and for heulandite. Zeo-

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shown in A (Arrows shown again = Mo 1, 2 and 3). It is clear that Mo1 was formed over the heulandite minerals present, indicating that its formation definitely postdates this of heulandite minerals. The mordenite earlier shown in Figures 3B and 3D (Figure 3D is an enlargement of Mo3) developed from the same precursor. Mo = mordenite.
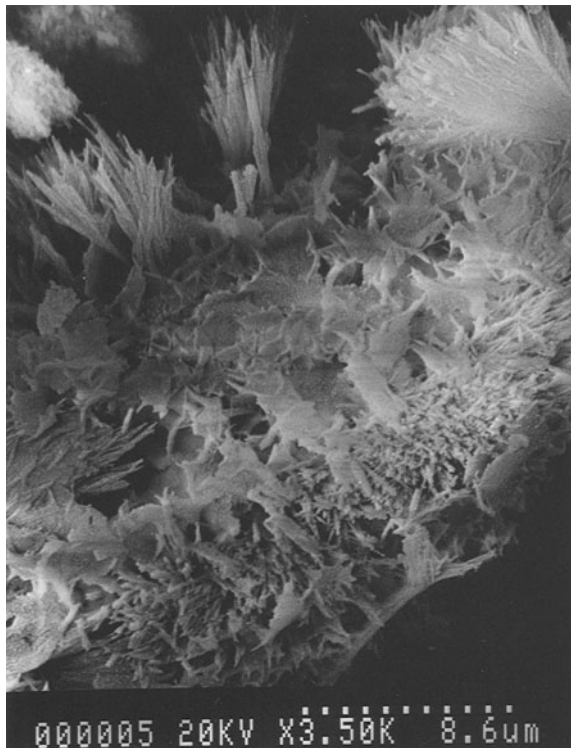
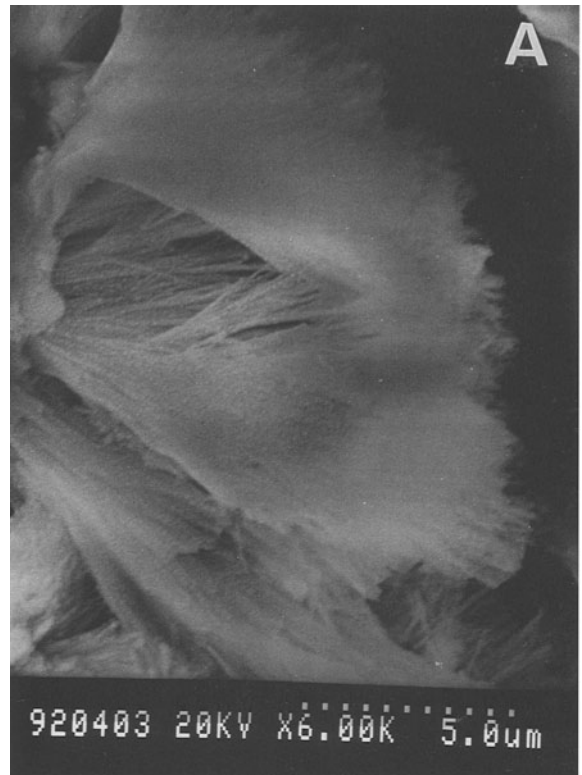Figure 12.   Bundles of radiating mordenite developed from an I–S material.

litization is often controlled locally, sometimes within the area of individual glass shards and pumice fragments. Parts of this gel-phase could have remained unaltered within small closed systems and did not react to smectite and/or clinoptilolite. Tsolis–Katagas and Katagas (1989) showed that for areas where there is no vertical or lateral zonation, irregular distribution of assemblages can be attributed to variations in heat flow, ionic activity of interstitial waters and permeability. They also believe that the formation of authigenic phases can impose barriers to permeability and subdivide an open system into smaller closed systems. At Polyegos, some very small quantities of mordenite could have formed within small closed systems from these pre-existing gel-like types of materials.

There is no evidence to support the formation of mordenite directly from the dissolution of the glass prior to or concurrently with the heulandite minerals. There was a small amount of mordenite (Figures 3C and 13) that is believed to have formed from a gel-like type of material.

Illitization of Smectite

Under the same conditions of increasing temperature and changing pore chemistry that favor the transformation of heulandite minerals to mordenite, initial smectite phases were partially reacted to I–S and ultimately to illite. The differences in the occurrence of

Figure 13.   A and B) Mordenite developing on a gel-like type of material. The mordenite earlier shown in Figure 3C also developed from a similar precursor.

I–S and illite phases within the area and the lack of any zonal variation indicates that a general increase in temperature throughout the area was the driving force for the illitization of smectite. However, the degree of the illitization of smectite (illite content in I–S layers) was found to vary from place to place, probably depending on temperature; possibly on fluid composition, too. It seems that in some cases it was locally controlled by the circulation of the hydrothermal fluids. Around barite veins and flats and when illite is not the only phase present, illite content in I–S mixed layers is very high, with samples taken near barites, having 70 to about 90% illite. The relation of temperature to the illitization of smectite is obvious, as the percentage decreases with increasing distance from the barite veins. Therefore, illitization was initiated by a general temperature increase in the area, but the emplacement of barite deposits locally provided some extra heat. Kalogeropoulos and Mitropoulos (1993) showed that the temperature of barite veins from the neighboring island of Milos was from 140 to 170 °C, a temperature more than adequate to initiate the illitization of smectite.

Illite–smectite-to-illite reaction has been recorded in many diagenetic environments (Perry and Hower 1970; Hower et al. 1976; Boles and Franks 1979; Bell 1986; Keller et al. 1986; Ramseyer and Boles 1986; Ransom and Helgeson 1989; Lanson and Champion 1991; Buatier et al. 1992). Perry and Hower (1970), Hower et al. (1976), Boles and Franks (1979) and Lanson and Champion (1991) found that the proportion of the smectite interlayers in I–S decreases with depth. The I–S-to-illite reaction has been also recorded in other geological settings, including contact metamorphism (Nadeau and Reynolds 1981), thrust sheet burial areas (Hoffman and Hower 1979) and hydrothermal alteration systems (Inoue et al. 1987; Inoue et al. 1988; Inoue et al. 1992). During hydrothermal experiments, it was shown that the expandability of the I–S phase decreased rapidly at first and then asymptotically approached a constant value at long run times (220 d). In general, the expandability decreased with increasing temperature. At 250 °C, the expandability was stabilized at 45%, and at 450 °C it had been reduced to 4% (Whitney and Northrop 1988).

CONCLUSIONS

The pyroclastics formation of Polyegos Island, Greece, occurs in 2 different units, the Prassa ignimbrite and the Myrsini pyroclastics, reflecting different eruption events. In Polyegos, mordenite has been identified by means of XRD and SEM to dominate the mineralogy of the pyroclastics from the northern exposure of the Prassa ignimbrite. It is one of the few cases where mordenite can be found in percentages up to 90% as the dominant phase produced by alteration of volcaniclastic materials. Clinoptilolite (heulandite

type 3) was found in very few samples, throughout the pyroclastic deposits. These intact clinoptilolite crystals were positively picked up by XRD and they were classified using thermal tests. In most cases, though, crystals of heulandite minerals were found to have suffered dissolution effects. At the same time, modernite was found draped along them, resulting from the alteration of heulandite minerals. The initial authigenic mineralogy was dominated by the heulandite minerals and the majority of Polyegos mordenite was formed during hydrothermal alteration of the heulandite minerals. Some mordenite has been found to have been formed from I–S phases. There is no strong evidence found to correlate the formation of mordenite with the initial dissolution of the glass, other than some very minor amount of filiform mordenite, which was found to have been formed from a gel-like type of material. The higher temperature that favors mordenite over heulandite minerals was provided by the intrusion of rhyolitic bodies into the area. The circulation of hydrothermal fluids associated with the volcanic activity, which had probably mixed with seawater, provided the means of interaction and the extra Na that is required for the formation of mordenite. The absence of analcime and/or albite indicated that the Polyegos mordenite was formed under a pH <12, and at high temperature and high Na^+ concentration conditions, but not high enough to form analcime and/or albite.

ACKNOWLEDGMENTS

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