

MINERALOGICAL CONSTRAINTS TO THE FORMATION OF VEIN-TYPE ZEOLITES FROM KIZARI AREA, THRACE NORTHERN GREECE

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Abstract

Vein-type zeolites in Kizari area, (western Thrace) are found within fresh to zeolitic altered volcanic rocks of andesitic to dacitic composition. The zeolites stilbite-Ca, Sr-bearing heulandite-Ca and laumontite occur in epithermal-style crustiform quartz/chalcedony-calcite veins crosscutting lavas and volcanic breccias. Open-space filling is common and well-shaped crystals (up to 3cm) were observed. Smectite, feldspar, magnetite, pyrite and rutile occur in minor amounts in the veins. Halite and barite grains are included in stilbite-Ca. SEM-EDS data indicate high Sr (up to 4.4 wt. % SrO) and Ba (up to 2.9 wt. % BaO) contents for heulandite-Ca. It is suggested that the studied zeolites are intergral parts of the porphyry-epithermal mineralizing systems which operated in the area during the Oligocene. Their formation took place in the outmost transitional propylitic to fresh zones of the porphyry-epithermal systems and in a submarine environment as indicated by the geological and mineralogical evidence.

Key words: vein-type zeolites, stilbite-Ca, Sr-bearing heulandite-Ca, laumontite, submarine.

1. Introduction

Exploration activities during the last two decades in western Thrace resulted in the discovery of several zeolites deposits hosted mainly in Tertiary volcanoclastic rocks at Petrota, Pentalofofos, Metaxades, Lefkimi, Ferres and Skaloma regions (Kossiaris et al., 1987; Marantos et al., 1989; Tsolis-Katagas & Katagas, 1990; Karafoti & Arikas, 1990; Tsirambides et al., 1989, 1993; Filippidis, 1993; Skarpelis et al., 1993, 1995; Kitsopoulos & Dunham, 1994; Stamatakis et al., 1996, 1998; Kirov et al., 1999; Hall et al., 2000; Kassoli-Fournaraki et al., 2000; Marantos, 2004; Perraki & Orfanoudaki, 2004; Filippidis and Kantiranis, 2005). The most common zeolites present in western Thrace are of HEU type (heulandite-clinoptilolite), but minor amounts of mordenite, analcime, stilbite and laumontite also occur. According to the above authors, the zeolites were formed from the alteration of volcanic glass, and are accompanied by clays, silica polymorphs (quartz, cristobalite), feldspars and calcite.

In addition, vein-type zeolites occur in a few localities (e.g. Virini, Feres, N. Santa and Vathi/Kilkis) (Michael et al., 1984; Filippidis et al., 1988; Marantos et al., 2004, 2007), and show similarities to hydrothermal zeolites found in many parts of the world (e.g. Ferroe islands/Danemark, Nova Scotia/Canada, Fassatal/Italy, Baical/Siberia, Andreasberg/Germany, Teschen/Czech Republik, Kongs-

berg/Norway, Tergahorn/Island, Troodos Complex/Cyprus and Nasik, Poona/India (Extra Lapis, 2007).

Contrary to the papers published on the mineralogy, petrology and geochemistry of western Thracian zeolitized volcanoclastic deposits, there is limited information on the formation of vein-type zeolites in Thrace and in Greece in general. This study describes a new occurrence of vein-type zeolites in western Thrace, located within an andesite quarry at Kizari/Sapes in Rhodope prefecture, and present a model for their genesis based on mineralogical, mineral-chemical and geological data.

2. Regional geology

The geodynamic evolution of northeastern Greece includes an early oceanic-continental subduction/collision, growth of the thickness of the crust, and post-collisional extensional collapse of the orogen resulting in the formation of several supra-detachment basin-controlled volcanosedimentary formations from the Lutetian (48 - 43Ma) through the Oligocene up to the Pliocene (Krohe & Mposkos, 2001; Papadopoulos & Anastasiadis, 2003). Slab break-off and/or slab delamination were principal mechanisms for the generation of extensive post-collisional magmatism in the area (Pe-Piper et al., 1998). The resulting plutonic-subvolcanic and volcanic rocks in Evros-Rhodopi region show calc-alkaline, high-K calc-alkaline, to shoshonitic affinity (Papavasiliou & Sideris, 1984; Innocenti et al., 1984; Eleftheriadis, G., 1995; Christofides et al., 2004; Magganas et al. 2004). For the basic to intermediate and acid magma generation an enriched mantle source region, extensive differentiation within the crust, subordinate magma mixing and/or a partial melting of crustal material has been documented. The main phase of the Tertiary magmatism took place during the Oligocene and is represented by submarine/terrestrial volcanics and subvolcanic rocks associated with volcanosedimentary series composed of marls, sandstones, clays and intercalations of volcanic rocks (lavas, tuffs, pyroclastics).

Numerous porphyry Cu-(Mo) and epithermal Au-Ag-type systems formed during the Tertiary magmatic event in northeastern Greece, and are genetically related to microdiorite, microgranite, andesite and the dacite porphyries (Arikas & Voudouris, 1998; Melfos et al., 2002). Faults and veins trending NW-SE, NE-SW and NNW-SSE influenced the distribution of magmatic rocks and spatially related magmatic-hydrothermal mineralization.

3. Local Geology

The Kizari area belongs to the eastern part of Komotini basin and also forms the northern extension of the eroded Tertiary volcanic edifice of Konos/Sapes: the Tertiary volcanosedimentary formations consist of M-U Eocene conglomerates, sandstones, marls, tuffs and tuffites, overlain by an Oligocene volcanic sequence dominating the entire area of Konos-Kizari (Fig. 1). The later consists of pyroclastics, lava flows and domes of andesitic to dacitic composition. Two types of intrusive stocks have been recognized in the broad area: an older, hydrothermally altered dacite stock with porphyry/epithermal-type mineralization at Konos area (Voudouris et al., 2006; Orтели et al., 2009) and the 32 Ma (Del Moro et al., 1988) quartz monzodiorite of Kirki. The majority of magmatic rocks in the Kizari-Konos area are hydrothermally altered as a result of repeated hydrothermal activity during the lifespan of the above mentioned porphyry-epithermal system. Alterations typical of both high-sulfidation- and low-sulfidation epithermal gold deposits are the products of interaction between rocks and fluids of acid and near-neutral to alkaline pH respectively (Voudouris, 1993). These alterations are fault-controlled and related mainly to the N-S and E-W trending faults in the area. The western part of the studied area is covered by the Silver Hill conglomerate (Shaw & Constan-

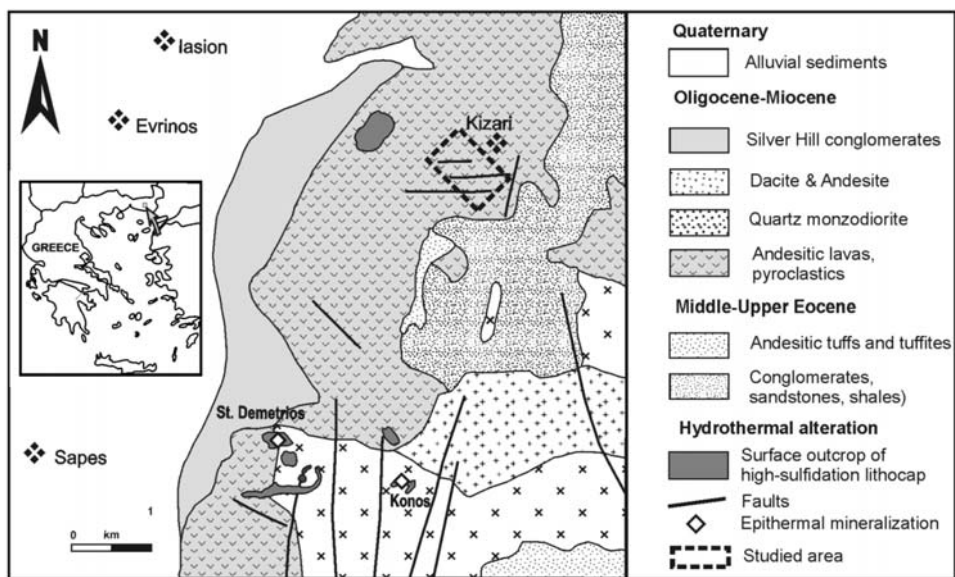


Fig. 1: Simplified geological map of Sapes-Kizari area and location of studied area (open square) (modified after Bitsios, 1973; Arikas, 1980; Greenwich Resources plc, 2004; Ortelli et al. 2009).

tinides, 2001), composed of angular to subrounded fragments of advanced argillic altered volcanic rocks and quartz-amethyst veins within an argillic matrix (Fig. 1). According to Shawh & Constantinides (2001) the Silver Hill conglomerate represents a mass flow deposited marginal to the Komotini Graben during its subsidence.

4. Description of the vein-type zeolite occurrences

The dominant rock types in the studied area are pyroxene-hornblende-bearing andesites, as well as volcanic breccias. The zeolite-bearing veins are fault-related and occur within E-W and N-S trending veins, which crosscut andesitic lavas and volcanic breccias in the broad area (Fig. 2). Fresh andesitic lavas consist of plagioclase, clinopyroxenes and hornblende phenocrysts embedded within a groundmass (up to 70 vol. %) containing microliths of the above minerals surrounded by a glassy matrix. Magnetite occurs both as phenocrysts and disseminated in the matrix. The volcanic breccias contain up to dm andesite angular to subrounded fragments within a fine-grained tuffitic matrix. The breccia fragments are identical to the above mentioned porphyritic lavas, whereas the matrix of the breccias is holocrystalline but finer grained compared to the fragments. Both the groundmass of the fragments and the matrix, consist of plagioclase and pyroxene microliths, few K-feldspar and devitrification products of the glassy matrix.

The volcanic rocks are relatively fresh and only in the vicinity of the zeolite-bearing veins, are partially altered to smectite, pyrite, magnetite, calcite, silica polymorphs and zeolites. The above secondary minerals occur either finely disseminated in the groundmass or as replacement of the phenocrysts. The veins show typical epithermal structures as open space filling and crustification banding. They reach lengths of up to several meters and are up to 50cm wide. Vein mineralogy greatly varies within the studied area and mainly two types of veins are distinguished: quartz-chalcedony±stilbite (Fig. 2b), and carbonate-rich stilbite-laumontite veins (Fig. 2c to f). The last vein-

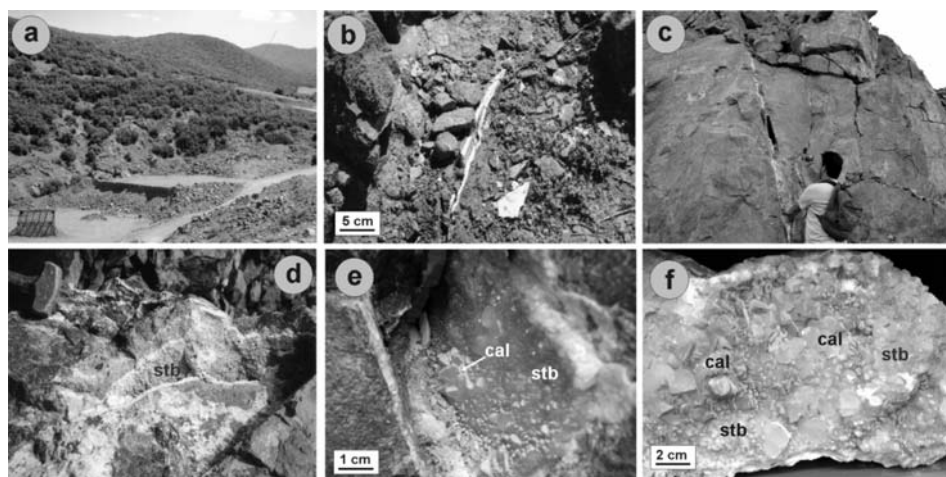


Fig. 2: (a) Panoramic view of lava quarry at Kizari (August 2006); (b) Chalcedony-stilbite veins crosscutting zeolitic altered lavas at Kizari (August 2006); (c) Stilbite-calcite veins with open-space filling crosscutting lavas (August 2009); (d, e) Stilbite (stb) and calcite (cal) filling fissures within lavas; (f) Hand-specimen with orange-colored stilbite (stb) and green-colored calcite (cal).

type may also be monomineralic (stilbite- or laumontite only) or may contain alternating bands with the above mentioned minerals. The quartz-chalcedony-rich veins (up to 5cm wide) are banded with initial deposition of white-colored chalcedonic silica and final deposition of colourless chalcedony and fine-grained quartz. Open spaces are filled by pale orange to beige-colored idiomorphic stilbite crystals and very minor calcite.

In the carbonate-rich veins the silica polymorphs are missing and vein deposition starts with minor calcite, followed by laumontite, stilbite and finally by green-colored calcite (Fig. 2e, f). Hydrothermal breccias are common and consist of fragments of volcanic rocks surrounded by a stockwork of zeolite-bearing veinlets and veins.

5. Methods

Twenty three thin and polished thin sections of host rocks and zeolite assemblages were studied with an optical microscope and a JEOL JSM 5600 scanning electron microscope equipped with back-scattered imaging capabilities, at the Department of Mineralogy and Petrology, University of Athens, Greece. Analytical methods also included X-powder diffraction measurements obtained using a SIEMENS type D-500 diffractometer with Cu tube and Co filter at the Department of Mineralogy and Petrology, University of Athens, Greece. The definition of the studied zeolites is based on the nomenclatures for zeolite minerals proposed by Coombs et al. (1998).

6. Mineralogy and mineral-chemistry

6.1 Zeolite minerals

Stilbite: Stilbite with ideal formula $\text{Na,Ca}_4(\text{Al}_9\text{Si}_{27}\text{O}_{72})\cdot 30\text{H}_2\text{O}$ is the most abundant mineral in the veins at Kizari quarry. It occurs in both silica- and carbonate-rich veins as euhedral crystals up to 3cm

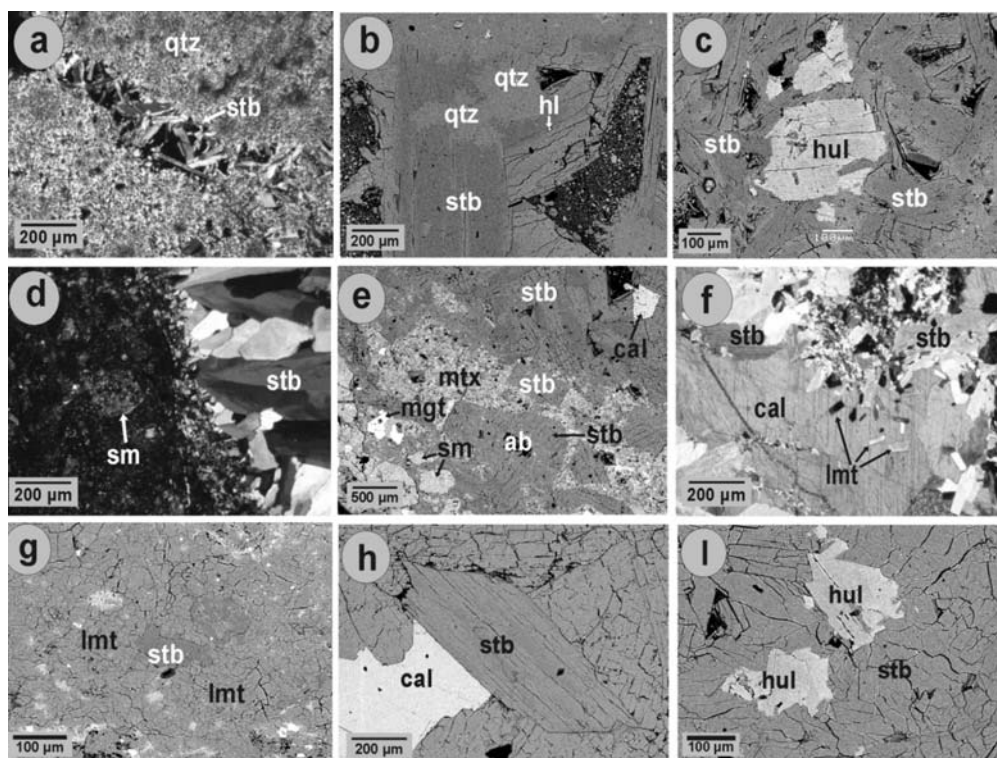


Fig. 3: Microphotographs of the quartz-chalcedony±stilbite veins (a-c) and carbonate-rich stilbite-laumontite veins (d-i) at Kizari (a) Stilbite (stb) filling vugs in quartz (qtz) veinlet (polarizing microscope image, +nicols); (b) Stilbite (stb) with halite (hl) inclusions, surrounds quartz (qtz) (SEM-BSE image); (c) Sr-bearing heulandite-Ca (hul) replaced by stilbite (stb) (SEM-BSE image); (d) Stilbite (stb) veinlet in weakly altered andesite. Smectite (sm) is pseudomorph after pyroxene phenocrysts (polarizing microscope image, +nicols); (e) Stilbite (stb), smectite (sm), albite (ab) and magnetite (mgt) replace plagioclase and clinopyroxene phenocrysts of andesite and also occur in the recrystallized groundmass (mtx). Stilbite and calcite (cal) also occur in veinlets (SEM-BSE image); (f) Laumontite (lmt) postdates stilbite (stb) and is surrounded by calcite (cal) (polarizing microscope image, +nicols); (g) Laumontite (lmt) replaces stilbite (stb) (SEM-BSE image); (h) Idiomorphic stilbite (stb) crystals overgrown by calcite (cal) (SEM-BSE image); (i) Sr-bearing heulandite-Ca (hul) replaced by stilbite (stb) (SEM-BSE image).

with well developed {110}, {010} and {001} faces. In the quartz-chalcedony veins stilbite post-dates silica polymorphs deposition, and filling fractures and open spaces in quartz or is overgrown on quartz (Fig. 3a to c). It contains small inclusions of halite (Fig. 3b) and barite and also replaces Sr-Ba-bearing heulandite-Ca (Fig. 3c). In the carbonate-rich veins stilbite surrounds albite in pseudomorphs after plagioclase (Fig. 3e), replaces and is replaced by laumontite (Fig. 3g) and similarly to the quartz-chalcedony veins also replaces Sr-Ba-bearing heulandite-Ca (Fig. 3i). Stilbite is overgrown by calcite (Fig. 3f, h). Its composition is close to stoichiometry with some K and Sr (up to 0.4 apfu) substituting for Na and Ca in the extra-framework sites (Table 1, Fig. 4). XRD patterns of stilbite are shown in Figure 5.

Table 1. Representative EPMA data of laumontite (1-2), stilbite (3-6), heulandite (7-10) and smectite (11-12)

	1	2	3	4	5	6	7	8	9	10	11	12
SiO ₂	52.38	52.72	55.91	58.03	58.77	56.83	55.66	56.36	57.42	57.66	34.82	33.51
Al ₂ O ₃	20.06	20.64	14.88	15.25	14.61	15.15	16.80	14.92	15.55	15.14	13.57	13.64
Fe ₂ O ₃	0.09	0.18	bd	bd	bd	bd	bd	bd	bd	bd	18.10	19.27
MgO	0.13	0.10	0.04	bd	0.12	bd	bd	bd	bd	bd	18.77	18.67
MnO	0.03	0.05	0.06	bd	0.07	0.01	bd	0.05	0.02	bd	0.31	0.23
CaO	9.54	9.56	6.83	7.32	7.03	7.79	4.89	4.23	4.62	3.99	1.65	1.02
Na ₂ O	0.84	1.14	1.56	0.76	1.22	0.94	1.20	0.75	1.13	1.15	0.39	0.34
K ₂ O	0.72	0.69	0.52	0.08	0.24	0.03	0.53	1.02	0.59	1.33	0.14	0.18
SrO	1.28	0.81	0.57	1.05	0.39	1.39	4.42	2.83	3.67	2.98	0.30	1.08
BaO	0.01	bd	bd	0.01	bd	bd	1.27	2.89	0.75	1.56	0.11	bd
Total	85.08	85.83	80.37	82.50	82.46	82.14	84.77	83.06	83.75	83.81	86.43	86.01
	48(O)	48(O)	72(O)	72(O)	72(O)	72(O)	72(O)	72(O)	72(O)	72(O)	22(O)	22(O)
Si	16.44	16.38	27.27	27.45	27.72	27.27	26.64	27.45	27.27	27.54	5.56	5.42
Al	7.44	7.56	8.55	8.55	8.10	8.55	9.45	8.55	8.73	8.55	2.56	2.61
Fe	-	0.06	-	-	-	-	-	-	-	-	2.17	2.34
Mg	0.06	0.06	-	-	0.09	-	-	-	-	-	4.45	4.51
Mn	-	-	-	-	-	-	-	-	-	-	0.06	0.03
Ca	3.24	3.18	3.60	3.69	3.60	3.96	2.52	2.25	2.34	2.07	0.28	0.17
Na	0.54	0.66	1.44	0.72	1.08	0.90	1.08	0.72	1.08	1.08	0.11	0.11
K	0.30	0.30	0.36	0.09	0.18	-	0.36	0.63	0.36	0.81	0.03	0.03
Sr	0.24	0.12	0.18	0.27	0.09	0.36	1.26	0.81	0.99	0.81	0.03	0.11
Ba	-	-	-	-	-	-	0.27	0.54	0.18	0.27	0.00	-

bd: below detection limit, Number of cations on the basis of oxygen (O)

Laumontite: Laumontite with ideal formula $\text{Ca}_4(\text{Al}_8\text{Si}_{16}\text{O}_{48}) \cdot 18\text{H}_2\text{O}$ is a very common constituent at Kizari quarry. It is found in the matrix of hydrothermal breccias, surrounding angular fragments of andesites, and in the carbonate-rich stilbite veins. It forms white-colored acicular crystals (up to 1cm) with well-developed the {110}, {100} and {001} faces. Laumontite predates and also postdates the deposition of stilbite-Ca. The chemistry of the analyzed laumontites is very close to the stoichiometric formula. The chemical analyses show a constant Si/Al ratio (Fig. 4). Small amounts of extra-framework cations (Na up to 0.7 apfu, K up to 0.3 apfu and Sr up to 0.24 apfu) substitute for Ca (Table 1, Fig. 4). An XRD pattern of laumontite is shown in Figure 5b.

Heulandite: Heulandite series minerals with general formula $(\text{Ca}_{0.5}, \text{Sr}_{0.5}, \text{Ba}_{0.5}, \text{Mg}_{0.5}, \text{Na}, \text{K})_9$

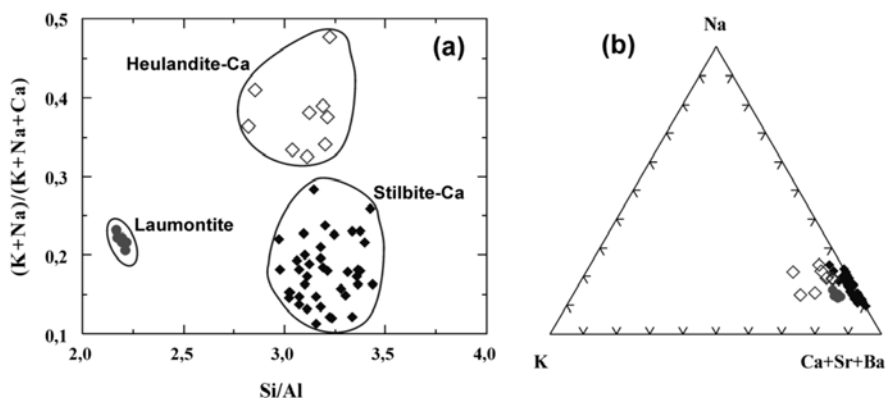


Fig. 4: Plot of zeolite compositions in terms of (a) $(K+Na)/(K+Na+Ca)$, and (b) in the ternary Na-K-(Ca+Sr+Ba) diagram.

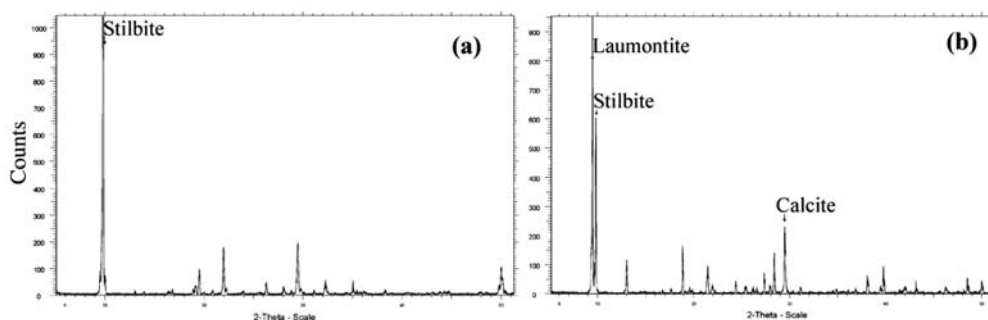


Fig. 5: X-ray diffractograms of (a) stilbite and (b) laumontite-stilbite-calcite association from Kizari.

$(Al_9Si_{27}O_{72}) \cdot 24H_2O$ display highly variable cation content, whereas Ca-, Na-, K-, Sr- and Ba-dominant compositions are known as heulandite-Ca, heulandite-Na, heulandite-K and heulandite-Sr and heulandite-Ba respectively (Coombs, et al. 1998; Larsen et al., 2005). Minerals with the same framework topology but with $Si:Al \geq 4.0$ are distinguished as clinoptilolites (Coombs et al., 1998). In both quartz-chalcedony±stilbite, and carbonate-rich stilbite-laumontite veins heulandite occurs as inclusions (up to 400 μ m) in stilbite (Figs 3c, i). The analyzed heulandites contain up to 1.2 apfu Na, 0.8 apfu K, 1.3 apfu Sr and 0.5 apfu Ba, and are characterized as Sr-Ba-rich heulandites-Ca (Table 1, Fig. 4).

6.2 Smectite

Smectite is a common constituent of the altered volcanics, forming pseudomorphs after pyroxene and hornblende, together with magnetite, pyrite, rutile, calcite and stilbite (Fig. 3d, e). It is also disseminated in the recrystallized groundmass. Representative chemical analyses are given in Table 1. The analyzed smectites contain 13.9-18.77 wt. % MgO (corresponding to 3.55-4.51 apfu Mg) and 16.16-19.67 wt. % FeO (2.03-2.83 apfu Fe).

6.3 Carbonates, Sulfates

In the carbonate-stilbite-laumontite veins, calcite postdates zeolite deposition in open spaces (Fig. 3f,

h). Calcite in green colored crystals up to 5cm is common with both skalenohedral and rhombohedral habits present. In the quartz-chalcedony±stilbite veins minor calcite predates and also postdates quartz and stilbite deposition. In the volcanic wallrocks calcite occurs in phenocryst phudomorphs as well as finely disseminated in the groundmass. Microprobe analyses indicate very minor amounts of Mn, Fe and Mg (<0.1 wt. %). Barite is present as small inclusions in stilbite crystals in the same veins.

7. Discussion-Conclusions

Zeolites occur in rocks of different mineralogical composition, age and geological environment. According to their mode of occurrence and formation environment, mainly two groups of zeolite occurrences have been distinguished (Iijima 1980; Gottardi & Galli, 1985; Hay and Sheppard 2001): (a) those formed under diagenesis to very low-grade metamorphism and (b) hydrothermal genesis. According to Hay (1966), Bargar & Keith (1995), Chipera and Apps (2001), Sheppard and Hay (2001), Utada (2001), and Marantos et al. (2007), the formation and distribution of zeolites is controlled by three main factors: a) the composition of the hostrocks, b) the variation in temperature and pressure, and c) the chemistry of pore water. In general, zeolites are formed under relatively high activity of alkalis and alkali earth elements and high pH values.

Recent studies on southeastern Rhodope zeolites in Bulgaria and Greece suggested a hydrothermal model, where the zeolitization of the volcanoclastic rocks was caused by low-temperature open hydrothermal systems in a shallow-marine environment (Raynov et al., 1997; Sheppard and Hay, 2001; Yanev et al., 2006; Marantos et al., 2007).

The present study describes stilbite-Ca, Sr-bearing heulandite-Ca and laumontite in euhedral crystals up to 3cm associated with smectite, albite, magnetite, pyrite and rutile, within epithermal-style crustiform quartz/chalcedony-calcite veins crosscutting lavas and breccias. Based on geological, petrographical, mineralogical and geochemical data the studied zeolites are of hydrothermal origin and can be regarded as integral parts of the porphyry/epithermal systems in the area. The Kizari zeolites are considered to have been formed in the transitional zone between propylitic alteration and fresh rocks and in a submarine environment as indicated by the presence of halite. The fluids were supersaturated in SiO₂ as can be deduced from the presence of chalcedony and quartz in vugs and veins of the rocks. The observed rhythmic zoning suggests alternated/repeated deposition of zeolites, calcite and smectite at several stages.

The chemical composition of zeolites at Kizari (Ca-dominant) and the absence of Na-rich zeolites (e.g. analcime) may suggest a deeper environment of formation, since at depth the impact of sea water with Na as the main constituent was rather low during zeolitic alteration as in similar zeolite occurrences in basic igneous rocks of Troodos Complex, Cyprus (Dill et al., 2007). The formation of laumontite and stilbite at Kizari may be resulted from the nature of the hydrothermal fluids, which were more enriched in Ca, Ba and Sr. Minor K and Na amounts in the zeolites at Kizari, are derived from glass present in the groundmass of the volcanics. Laumontite and stilbite formation together with albite is attributed to Ca release during breakdown of plagioclase in the rocks. In addition calcium released by the decomposition of An-rich plagioclase was taken up by calcite. This mechanism is also proposed for the laumontite-stilbite association present in stockwork-like zeolitization in the basic igneous rocks of the Troodos Complex (Dill et al., 2007). According to Dill et al. (2007), laumontite is formed at low PH₂O, whereas at higher PH₂O stilbite may crystallize according to the following reactions: anorthite + quartz + 4H₂O → laumontite and anorthite + quartz + 7H₂O → stilbite. The studied zeolites were formed at relatively low temperatures (<140°C), since stilbite coexists with heulandite and laumontite between 110 and 120 °C (Bargar 1994), and in the Troodos Complex

stilbite has derived from laumontite as temperature and pressure dropped below about 140 °C (Dill et al. 2007). In zoned sequences of zeolites in amygdales and veins in the North Mountain Basalt, Nova Scotia, the succession of mordenite → heulandite → stilbite are interpreted as developing under falling temperatures by active hydrothermal circulation (Pe-Piper, 2000).

The amount of the Kizari zeolites is not feasible for exploitation, however the broad area should be considered as target for future exploration. Under consideration of their abundant zeolitic veins and alteration, the quarried lavas are probably not much suitable materials for construction purposes. Nevertheless, the studied zeolites may provide valuable mineralogical specimens suitable for museum collections and educational purposes. Based on this assumption, the Kizari quarry should be protected and considered as a visiting site in a broad Mineralogical-Petrological geotope in Rhodopi region.

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