

**Research Paper****MINERALOGICAL AND GEOCHEMICAL STUDY OF THE ZEOLITIZED  
VOLCANICLASTIC ROCKS OF PETROTA REGION, EVROS  
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[kantira@geo.auth.gr](mailto:kantira@geo.auth.gr)**Abstract**

The present work studies the tuffs associated with the volcanic area of the Paleogene Sheinovets caldera, located on the southeastern part of the Rhodope massif, in Bulgaria. Its purpose is to describe the mineralogical and geochemical composition of the zeolitized volcaniclastic deposits in the broader area of Petrota village, in the northwesternmost part of the Greek regional unit of Evros, in northeast Greece. The samples studied in this work were collected from seven (7) different locations, covering an area of almost 4 km in length and 2 km in width. Macroscopically, the samples display a greyish-green hue and they are widespread in the area of study. They often contain fragments of the crystalline metamorphic basement (mica-schists, phyllites, amphibolites, quartzites) and/or rhyolitic clasts. A rhyolitic outcrop of greyish-pink hue is observed in the Mavri Petra region, probably related to the Rupelian acid volcanism that occurred in the Sheinovets caldera. The mineralogy of the tuffs was studied under light polarizing microscope and using Scanning Electron Microscopy (SEM), and it was further confirmed by X-ray powder diffraction (XRPD) method. The initial matrix of the tuffs consisted predominantly of glass shards that are now partly or fully altered into zeolites and clay minerals, such as celadonite, displaying characteristic pseudomorphic structures. The dominant zeolite is clinoptilolite, while in some areas the presence of mordenite is also noticed. Feldspar phenocrysts are abundant, and they are represented by plagioclase and sanidine. Although quartz crystals can be observed under light-polarizing microscope solely in metamorphic fragments, the presence of silica polymorphs was also confirmed through SEM and XRPD analysis, with quartz and cristobalite prevailing. The mineralogical assemblage includes phenocrysts of biotite

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and in some cases amphiboles, while pyroxene, epidote, garnet, titanite, apatite, zircon, ilmenite, magnetite and rutile are additional minerals which have been identified locally in accessory quantities. Chemical analysis was carried out for major and trace elements, using the X-ray fluorescence (XRF) method and 4 Acid digestion ICP-MS analysis, respectively. The samples of Mavri Petra region, exhibit high concentrations in Cu, Pb, Mn, V, P and W. The analyzed concentrations of U in the area of Palaeokklisi are relatively high in comparison to the rest due to its proximity to a fault. Towards the northwestern study area, close to the Greek-Bulgarian border, the concentrations of Sr appear to be particularly high, probably because the area is closer to the volcanic centre.

**Keywords:** *zeolitization, clinoptilolite, argillic alteration, volcanoclastic rocks, Petrota, Evros*

### **Περίληψη**

Η παρούσα εργασία μελετά τους ηφαιστειακούς τόφφους που σχετίζονται με την ηφαιστειακή δραστηριότητα της Παλαιογενούς καλδέρας του Sheinovets, η οποία βρίσκεται στο νοτιοανατολικό τμήμα της Μάζας της Ροδόπης, στη Βουλγαρία. Σκοπός της είναι να περιγράψει την ορυκτολογική και γεωχημική σύσταση των ζεολιθοποιημένων ηφαιστειοϊζηματογενών αποθέσεων στην ευρύτερη περιοχή του χωριού των Πετρωτών, στο βορειοδυτικότερο άκρο του Νομού Έβρου, στη βορειοανατολική Ελλάδα. Τα δείγματα που μελετήθηκαν συλλέχθηκαν από επτά (7) διαφορετικές τοποθεσίες, και καλύπτουν μια επιφάνεια περίπου 4 km σε μήκος και 2 km σε πλάτος. Μακροσκοπικά, παρουσιάζουν υποπράσινη έως πράσινη χροιά κι εντοπίζονται σε ολόκληρη την περιοχή μελέτης. Συχνά περιέχουν θραύσματα του κρυσταλλοσχιστώδους μεταμορφωμένου υποβάθρου (μαρμαρυγιακοί σχιστόλιθοι, φυλλίτες, αμφιβολίτες, χαλαζίτες) ή/και τεμάχια ρυολιθικών σωματιδίων. Η ρυολιθική εμφάνιση που παρατηρείται την περιοχή της Μαύρης Πέτρας είναι γκριζορόδινου χρώματος, και φαίνεται να σχετίζεται με την όξινη ηφαιστειότητα που έλαβε χώρα στην καλδέρα Sheinovets κατά το Ρουπέλιο. Η ορυκτολογική σύσταση των τόφφων μελετήθηκε με πολωτικό μικροσκόπιο και με τη χρήση ηλεκτρονικού μικροσκοπίου σάρωσης (SEM), καθώς και με τη μέθοδο της περιθλασιμετρίας κόνεως ακτίνων-X (XRPD). Η αρχική θεμελιώδης μάζα των τόφφων αποτελούνταν κυρίως από θραύσματα ηφαιστειακού γυαλιού που πλέον είναι μερικώς ή και πλήρως εξαλλοιωμένα σε ζεόλιθο και αργιλικά ορυκτά, όπως ο σελαδονίτης, παρουσιάζοντας χαρακτηριστική ψευδομόρφωση σε ζώνες. Ο ζεόλιθος που κυριαρχεί είναι ο κλινοπιτιλόλιθος, ενώ σε κάποιες περιπτώσεις παρατηρείται τοπικά και μορνενίτης. Οι φαινοκρύσταλλοι αστρίων είναι άφθονοι και αντιπροσωπεύονται κυρίως από

πλαγιόκλαστο και σανίδινο. Παρόλο που οι κρύσταλλοι του χαλαζία μπορούν να παρατηρηθούν στο πολωτικό μικροσκόπιο μόνο μέσα στα μεταμορφικά θραύσματα, η παρουσία πολύμορφων του πυριτίου επιβεβαιώθηκε από τις αναλύσεις SEM και τη μέθοδο XRPD, με τον χαλαζία και τον χριστοβαλίτη να επικρατούν. Ο βιοτίτης εμφανίζεται συνήθως σε φαινοκρυστάλλους, ενώ σε κάποιες περιπτώσεις διαπιστώνεται και η παρουσία φαινοκρυστάλλων αμφιβόλου. Επιπλέον, ο πυρόξενος, το επίδοτο, ο γρανάτης, ο τιτανίτης, ο απατίτης, το ζιρκόνιο, ο ιλμενίτης, ο μαγνητίτης και το ρουτίλιο είναι τα επουσιώδη ορυκτά που εντοπίστηκαν σε πολύ μικρές περιεκτικότητες. Η χημική ανάλυση πραγματοποιήθηκε με τη χρήση της μεθόδου φασματοσκοπίας φθορισμού ακτίνων-X (XRF) και μέσω της διαλυτοποίησης με τέσσερα (4) οξέα, για τα κύρια στοιχεία και τα ιχνοστοιχεία, αντίστοιχα. Τα δείγματα της Μαύρης Πέτρας παρουσιάζουν υψηλές συγκεντρώσεις σε Cu, Pb, Mn, V, P και W, ενώ οι συγκεντρώσεις U στην περιοχή Παλαιοκλήσι είναι σχετικά υψηλές σε σχέση με τις αντίστοιχες αναλύσεις στις υπόλοιπες περιοχές μελέτης, γεγονός που θα μπορούσε να οφείλεται στο ρήγμα που εντοπίζεται ανατολικά της συγκεκριμένης θέσης δειγματοληψίας. Στο βορειοδυτικό κομμάτι της περιοχής μελέτης, κοντά στα Ελληνοβουλγαρικά σύνορα, οι συγκεντρώσεις Sr εμφανίζονται ιδιαίτερα υψηλές, πιθανόν λόγω της μικρής απόστασης από το ηφαιστειακό κέντρο.

**Λέξεις κλειδιά:** ζεολιθοποίηση, κλινοπιλόλιθος, αργιλική εξαλλοίωση, ηφαιστειοϊζηματογενή πετρώματα, Πετροτά, Έβρος

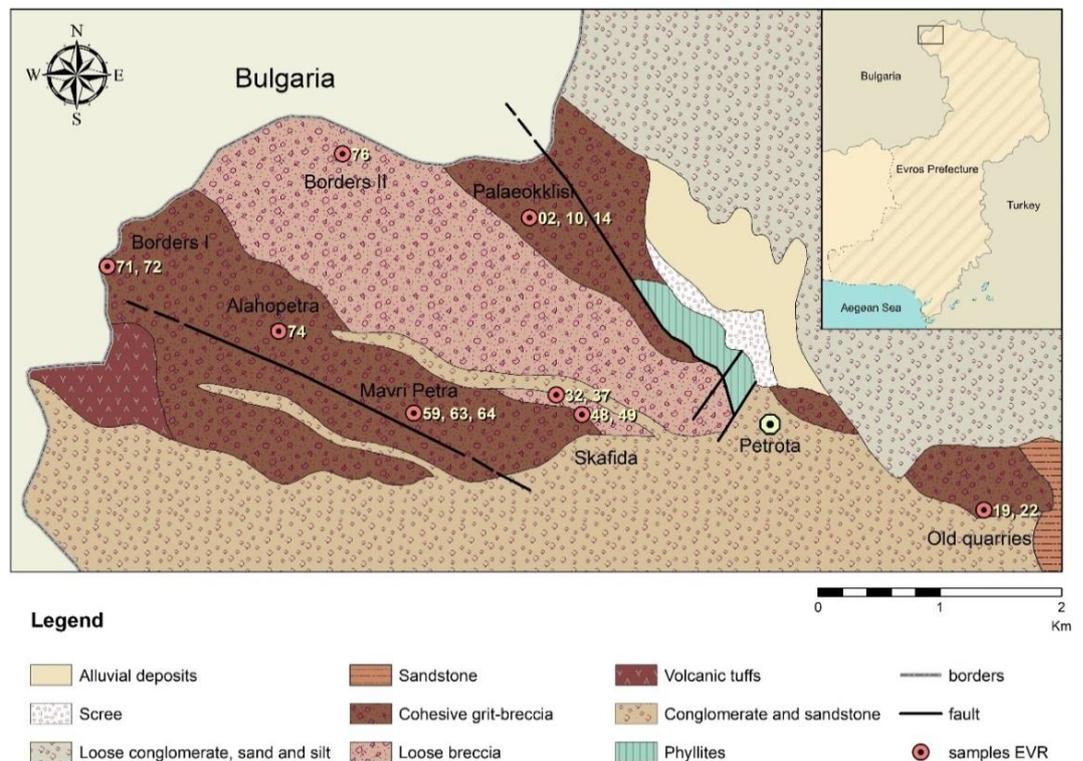
## 1. INTRODUCTION

The purpose of the present study is to describe the mineralogical and geochemical composition of the zeolitized volcanoclastic rocks in the area surrounding Petrota village, in the northwesternmost part of the Greek regional unit of Evros, in northeast Greece, in the context of the MSc Thesis of the first author. Several studies have already been published concerning the zeolitized rocks in the Greek part of the Rhodope massif (Kirov *et al.*, 1990; Tsolis-Katagas and Katagas, 1990; Tsirambides *et al.*, 1993; Filippidis *et al.*, 1995; Stamatakis *et al.*, 1996; Stamatakis *et al.*, 1998; Kassoli-Fournaraki *et al.*, 2000; Barbieri *et al.*, 2001; Perraki and Orfanoudaki, 2004; Marantos *et al.*, 2006; Filippidis *et al.*, 2007; Filippidis *et al.*, 2016a; Filippidis *et al.*, 2016b) and the corresponding occurrences in Bulgaria (Yanev *et al.*, 1989; Yanev and Bardintzeff, 1997; Yanev, 1998; Yanev *et al.*, 1998; Ivanova *et al.*, 2000, 2001; Georgiev *et al.*, 2002; Ivanova, 2005; Ivanova and Gier, 2006; Yanev *et al.*, 2006; Yanev and Ivanova, 2010). Even though the volcanism related to the corresponding formations in Bulgaria

has been thoroughly studied, any research conducted within the Greek borders is mainly focused on zeolites.

## 2. REGIONAL GEOLOGY

The study area covers the region between the Greek-Bulgarian borders and Petrota village (Fig. 1), that belongs geotectonically to the southeasternmost part of the Rhodope massif (RM). The northern boundary of the RM is defined by the Maritsa dextral strike-slip fault, while in the south, the synmetamorphic Rhodope nappe complex was affected by the subduction system related to the Vardar (Axios) Zone. The north-dipping Cretaceous subduction caused the genesis of the Sredna Gora Zone continental volcanic arc, located on the north of the Maritsa fault. As a result, southward-migrating magmatism occurred in several magmatic centres across the RM (Ivanov, 1960; Ricou *et al.*, 1998; Yanev *et al.*, 1989; Christofides *et al.*, 2004; Marchev *et al.*, 2004, 2005; Bonev *et al.*, 2013). According to Yanev *et al.* (1998), the volcanic activity in the southern Rhodopes took place in two main phases; the Upper Eocene (Priabonian) volcanic phase, from 37 to 35 Ma, and the Oligocene volcanic phase, from 34 to 24 Ma.



**Fig. 1:** Simplified geological map of the area around Petrota village, indicating the lithology and the sites of sampling and fieldwork.

According to Andronopoulos (1978), the RM is cropping out in a small area northwest of the Petrota village mainly composed of phyllites, schists and quartzites. The Komara series (Upper Eocene) are in direct contact with the probably Mesozoic metamorphic basement consisting mainly of conglomerate and coarse-grained sandstone. The Pentalofos sequence is represented by an outcrop of volcanic tuffs that overlies the Komara series near the Greek-Bulgarian borders. Their genesis is related to the volcanism within the Bulgarian portion of the RM and their age is considered to span from Priabonian to Lower-Middle Oligocene. Loose breccia and cohesive grit-breccia of the Upper Eocene complete the lithological assemblage of the Pentalofos sequence. A small portion of an upper sandstone series rich in fossils (corals and foraminifera) rests on the Pentalofos sequence. In the area of study, no other formations of the Palaeogene are exposed. The Plio-Pleistocene deposits are represented by loose conglomerate, sand and silt, often in alternating layers. Both the Upper Eocene conglomerate formation of the Komara series and the Plio-Pleistocene loose conglomerate assemblage, are widespread across the area of interest. On the north of Petrota village rest the Holocene scree and alluvial deposits (Fig. 1). According to Stamatakis *et al.* (1996, 1998), the zeolitic tuffs that rest on the pre-Cenozoic basement, extend on a horizon of 15km in length and 100m in depth. They are also highly fractured and with high porosity, therefore percolating groundwater and meteoric water preserve the open hydrologic regime active to this day.

## 2. ANALYTICAL METHODS

In order to determine the mineralogical composition of the zeolite-rich tuffs, six (6) polished thin sections were prepared and studied under a Carl Zeiss Axioscop 40 light-polarizing microscope, using objective magnification 5x, 10x and 20x and using a JEOL JSM-840A Scanning Electron Microscope (SEM) connected to an Energy Dispersive Spectrometer INCA 300 (SEM-EDS). The mineral phases of twelve (12) representative samples, were identified through the analysis of material grinded into fine powder by means of X-ray powder diffraction (XRPD), while the major chemical elements were analyzed by the X-ray fluorescence (XRF) method, using a Bruker S4-Pioneer XRF wavelength dispersive spectrometer. The preparation of the samples and their analysis took place in the laboratories of Aristotle University of Thessaloniki. Moreover, the same twelve (12) samples were studied through 4 Acid digestion ICP-MS bulk analysis at the laboratories of Bureau Veritas Commodities in Canada, in order to determine their concentrations in 35 trace elements. In order to identify the trace elements in the zeolitic tuffs, the 0.25 g split was heated in HNO<sub>3</sub>-HClO<sub>4</sub>-HF to fuming and taken to dryness. The residue was dissolved in HCl.

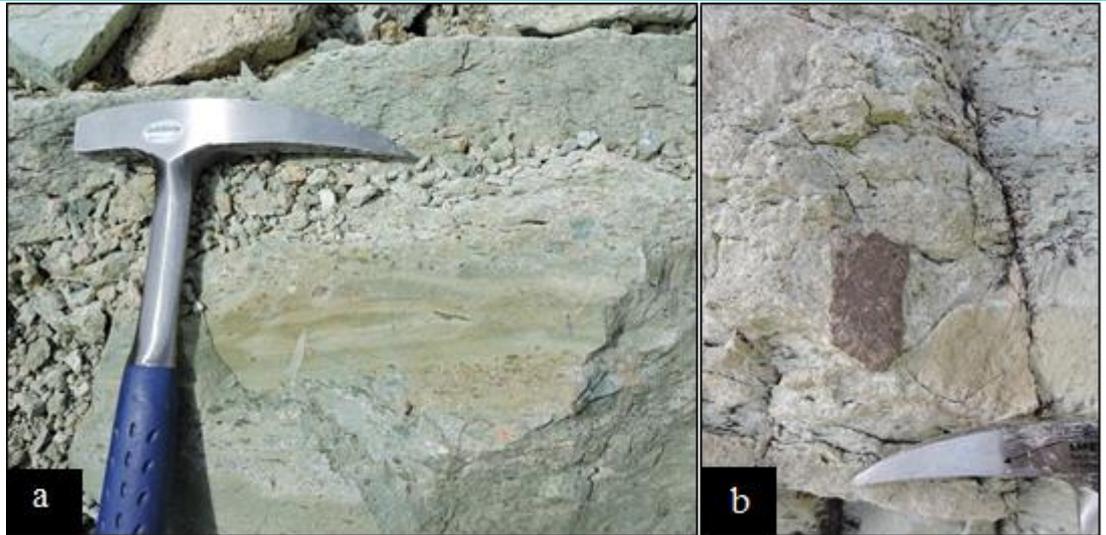
**Table 1.** Locations and analytical methods used for each sample.

Region	Sample	Polished thin section	XRPD analysis	XRF analysis	4 Acid digestion ICP-MS analysis	
Palaeokklisi	EVR02	-	✓	✓	✓	
	EVR10	-	✓	✓	✓	
	EVR14	✓	-	-	-	
Old quarries	EVR19	-	✓	✓	✓	
	EVR22	-	✓	✓	✓	
Skafida	North	EVR32	-	✓	✓	
		EVR37	-	✓	✓	
	South	EVR48	-	✓	✓	✓
		EVR49	✓	-	-	-
Mavri Petra	Rhyolite	EVR59	✓	-	-	
		Tuff	EVR63	-	✓	✓
Alahopetra	Tuff		EVR64	✓	✓	✓
		EVR74	✓	✓	✓	✓
Borders	I	EVR71	-	✓	✓	
		EVR72	✓	-	-	-
	II	EVR76	-	✓	✓	✓

### 3. RESULTS

#### 3.1. Petrology and Mineralogy

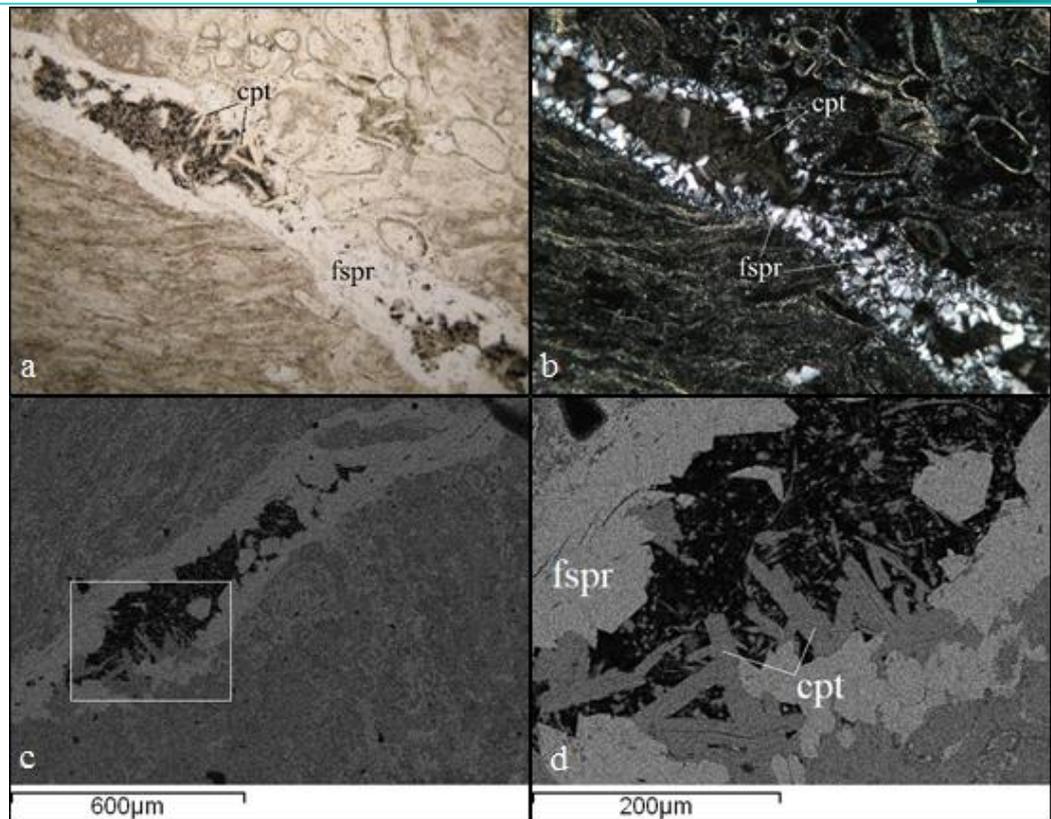
Macroscopically, all the zeolitized samples are greyish-green to deep green in colour, depending on the level of zeolitization and the concentration in clay minerals. The tuffs from Skafida area (EVR32, 37, 48, 49) display a deep green colour, while corresponding tuffs from the areas of Palaeokklisi (EVR02, 10, 14), Mavri Petra (EVR63, 64), Alahopetra (EVR74) and alongside the Greek-Bulgarian borders (EVR71, 72, 76), are generally paler or whitish (Fig. 2a), while the samples collected from the old quarries located southeastern of Petrota village (EVR19, 22) display a greenish-brown hue. One of the samples (EVR59) was collected from a rhyolitic outcrop in the Mavri Petra region and it also appears as clasts of various shapes and sizes in the green or whitish tuffs. This sample has a greyish-pink to greyish-red hue and appears to be less altered than the surrounding volcanic formations (Fig. 2b). Observation under light-polarizing microscope revealed clear differences among the samples examined due to their alteration level, matrix appearance and mineral composition.



**Fig. 2:** Macroscopic images of the zeolitized tuffs in the areas of Palaeokklisi and Mavri Petra, respectively. In Palaeokklisi area the tuffs have a distinctive pale grey-green hue (a), while in Mavri Petra the formation is whitish and rich in fragments, like the greyish-pink rhyolitic clast (b), detached from the rhyolitic outcrop in Mavri Petra.

Additionally, some of the samples contain fragments originated from the RM metamorphic basement, that present a wide variety in mineral composition and dimensions. The mineral assemblage of the fragments is dominated by quartz, K-feldspar, plagioclase, micas (muscovite and biotite), amphibole, pyroxene and garnet, and varies from area to area. Some of the crystals were detached from the clasts and can be found scattered within the matrix of the tuffs, often mistaken for phenocrysts of igneous affinity. Although most analytical methods indicate that quartz is abundant in all samples, no quartz phenocrysts could be identified microscopically. In most of the samples, feldspars phenocrysts are represented by plagioclase, often accompanied by sanidine. Moreover, they are often euhedral with distinctive zoning and twinning (after albite and Carlsbad laws).

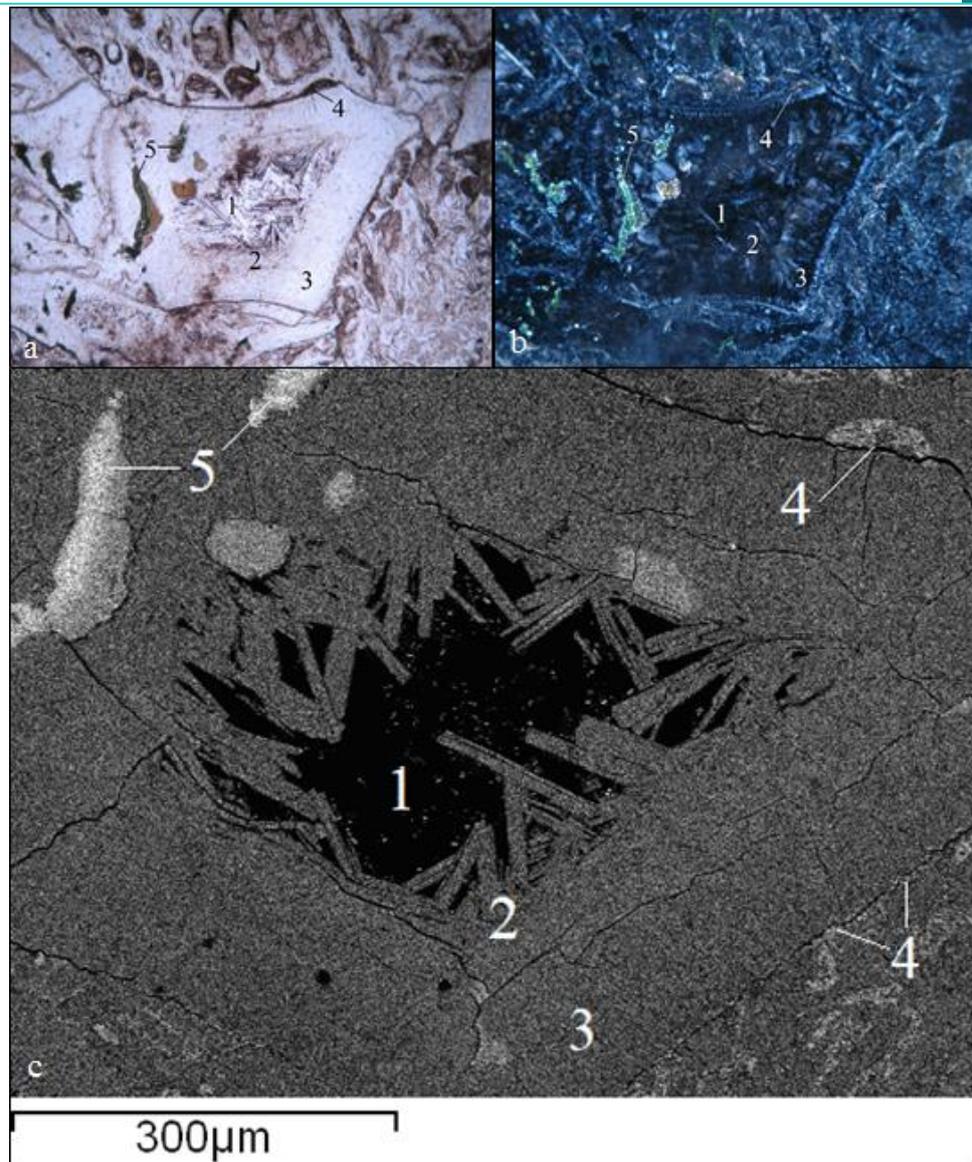
In particular, in the samples from Palaeokklisi (EVR02, 10, 14), the groundmass mainly consists of fine glass shards and argillic microphases aligned together, creating the impression of a flow (Figs 3a and 3b). The only phenocrysts in the matrix are plagioclase in rare apparitions, with very clear albite twinning. Although under the light-polarizing microscope clinoptilolite can solely be observed as idiomorphic tabular crystals that are developed on the walls of microcavities, its presence was noticed during SEM analysis in various domains of the thin sections and it was also confirmed through XRD analysis.



**Fig. 3:** Photomicrographs of tabular clinoptilolite (cpt) crystals and feldspar (fspr) aggregations, in a vesicle filling (sample EVR14), under (a) plane and (b) cross-polarized light; (c and d) the same mineral phases as depicted through SEM micrographs.

In the samples from Skafida (EVR32, 37, 48, 49) the glass shards have undergone argillic alteration, displaying characteristic pseudomorphic structures, as shown in Fig. 4. These structures occur when the tuffaceous deposits interact with percolating meteoric water or groundwater, in an open hydrologic system (Stamatakis, 1998; Sheppard and Hay, 2001).

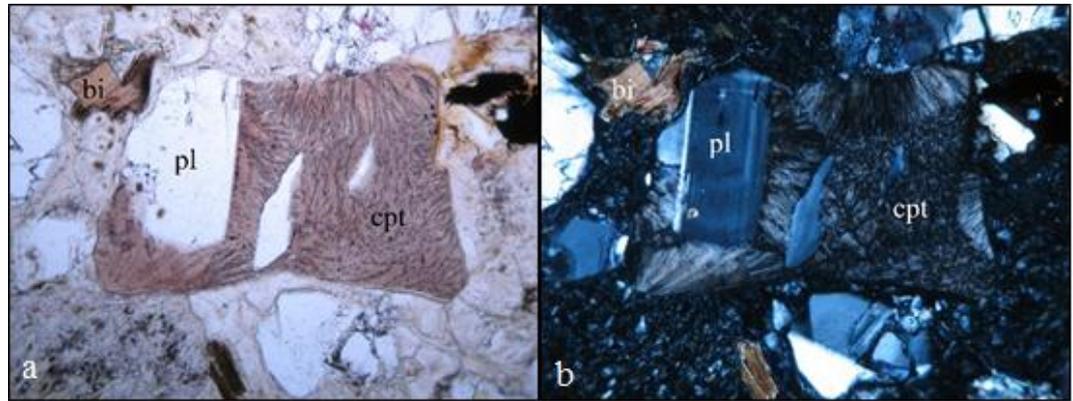
The samples also contain plagioclase and idiomorphic sanidine phenocrysts. The bent biotite and muscovite xenocrysts were detached from the mica-rich metamorphic fragments that can be found scattered among the altered glass shards. Apatite, garnet, ilmenite and zircon were traced in minor amounts through SEM.



**Fig. 4:** Detailed illustration of the pseudomorphic replacement of a glass shard in an extensively zeolitized tuff from Skafida region (sample EVR49) under plane-polarized (a), cross-polarized light (b) and through SEM (c). The central area (1) of the shard corresponds to an empty surface, where the euhedral tabular clinoptilolitic crystals (zone 2) are projected. Zone 3 represents a radial clinoptilolitic formation, hosting clay minerals, such as celadonite (5). The initial form of the glass shard is preserved but the peripheral zone is now replaced by a fine clay-coating (4).

The samples collected near the Greek-Bulgarian borders (EVR71, 72, 76) display a porphyritic microcrystalline texture and although the groundmass has undergone zeolitization, resulting in the genesis of pink clinoptilolitic formations (Fig. 5), which lack the typical pseudomorphic structures related with argillic alteration that were described above. The samples are rich in plagioclase and their phenocrysts are coarse-sieve textured. Both biotite and amphibole are abundant and exhibit strong pleochroism

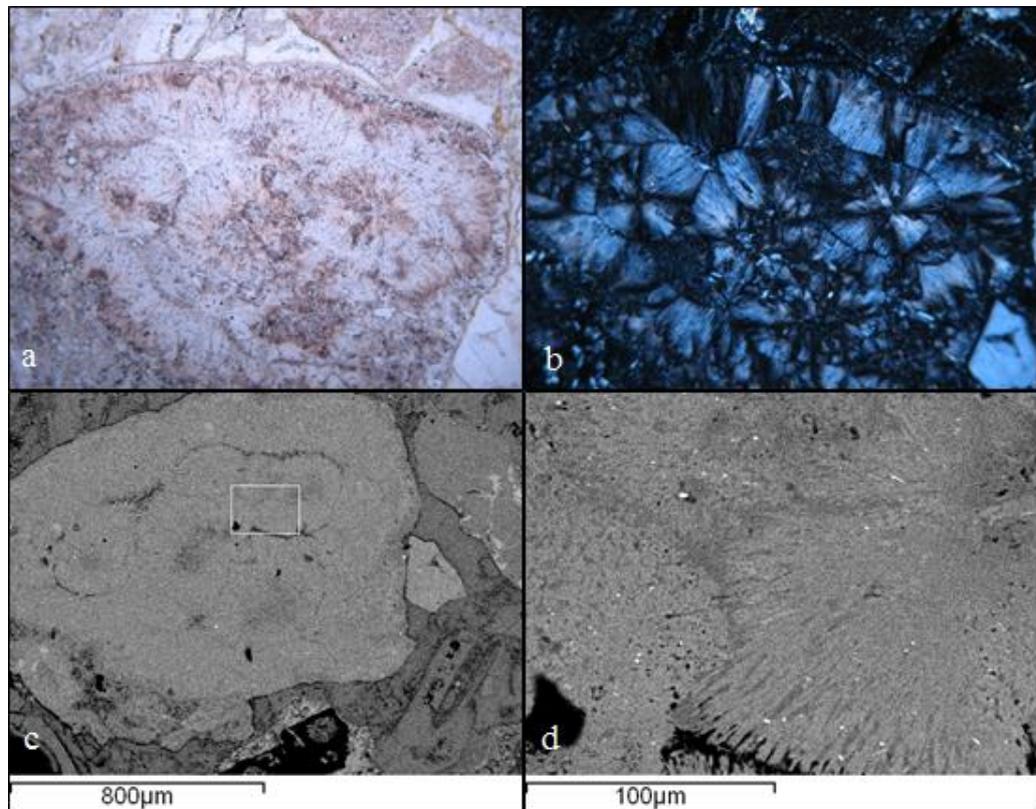
with pale to deep brown colour. Amphiboles are euhedral with excellent oblique cleavage and twinning. Pyroxene crystals can also be found, though only in small amounts. The mineralogical assemblage is completed with titanite, epidote, apatite, zircon, ilmenite and magnetite, that appear as accessory minerals. The XRPD analysis performed on the samples revealed the presence of mordenite.



**Fig. 5:** Photomicrographs of a clinoptilolitic aggregation (cpt) under plane-polarized (a) and cross-polarized light (b). Biotite crystals are brown and exhibit strong pleochroism (bi), while plagioclase often displays intense zoning and/or twinning (pl) (sample EVR72).

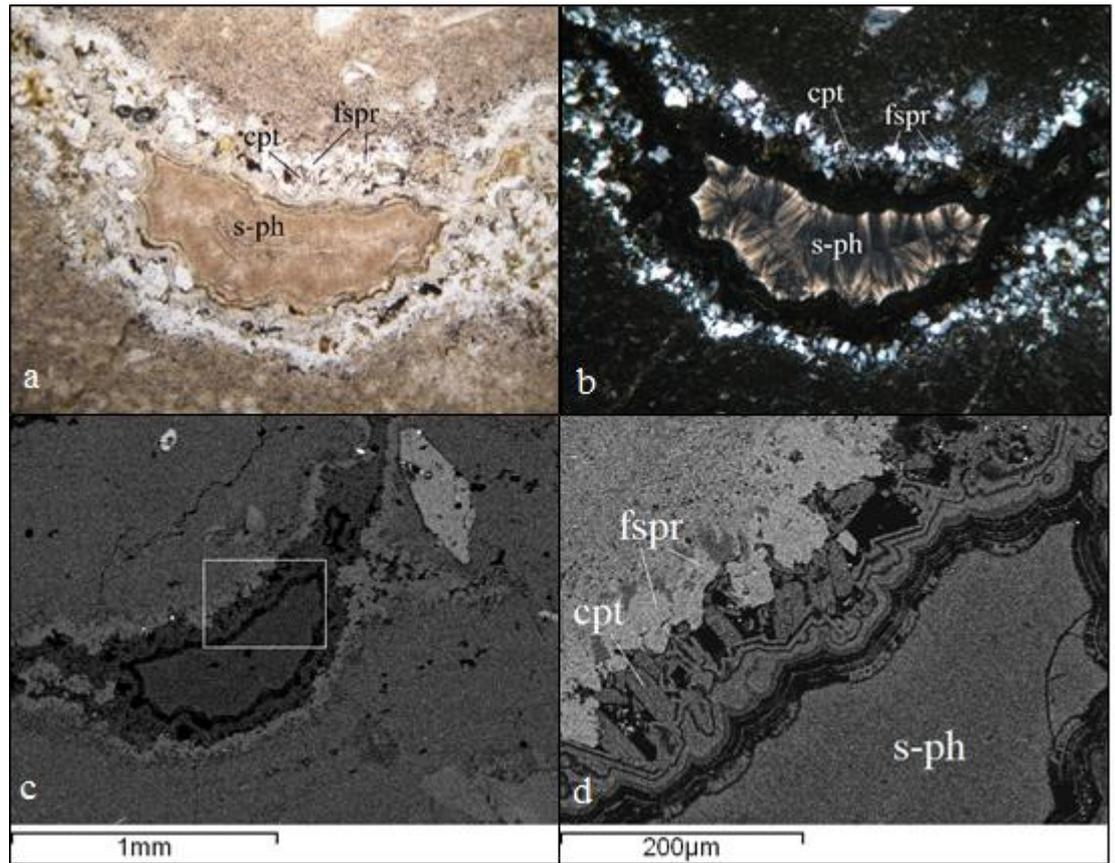
The sample collected from the area of Alahopetra (EVR74) has no pseudomorphic structures in the matrix, but zeolites (clinoptilolite and mordenite) were detected under SEM and through XRPD. The xenolithic fragments are mica-schists, mainly consisted of biotite, muscovite and quartz. Plagioclase is the dominant mineral under the light-polarizing microscope, while some rare apparitions of epidote were noticed. During SEM observation ilmenite, rutile and monazite crystals were traced. The data from SEM indicated that monazite crystals are rich in rare earth elements. The Mavri Petra samples can be divided into two groups: the zeolitized tuffs (EVR63, 64) and the rhyolitic outcrop (EVR59). The groundmass in the zeolitized tuffs is microcrystalline and it hosts phenocrysts and metamorphic fragments. The glass shards are locally altered into early pseudomorphic structures, less developed than those described in sample EVR49, from Skafida region. Spherulitic formations of clinoptilolite occur as a devitrification product of the volcanic glass shards, as shown in Fig. 6. The pyrogenic phenocrysts are mainly feldspar and biotite, with plagioclase crystals displaying intense zoning and twinning. Epidote phenocrysts are rare but present, probably originated by argillic phases during hydrothermal alteration, as its development follows the glass shard boundaries. The constituents of the metamorphic fragments are micas, feldspars, quartz garnet, but fragments with pyroxene or amphibole can also be found. Amphibole crystals from the

clasts can also be found scattered in the matrix. They exhibit intense pleochroism with a distinctive light-blue colour. Observation under SEM also revealed the presence of titanite, apatite and zircon, with high concentrations in Th.



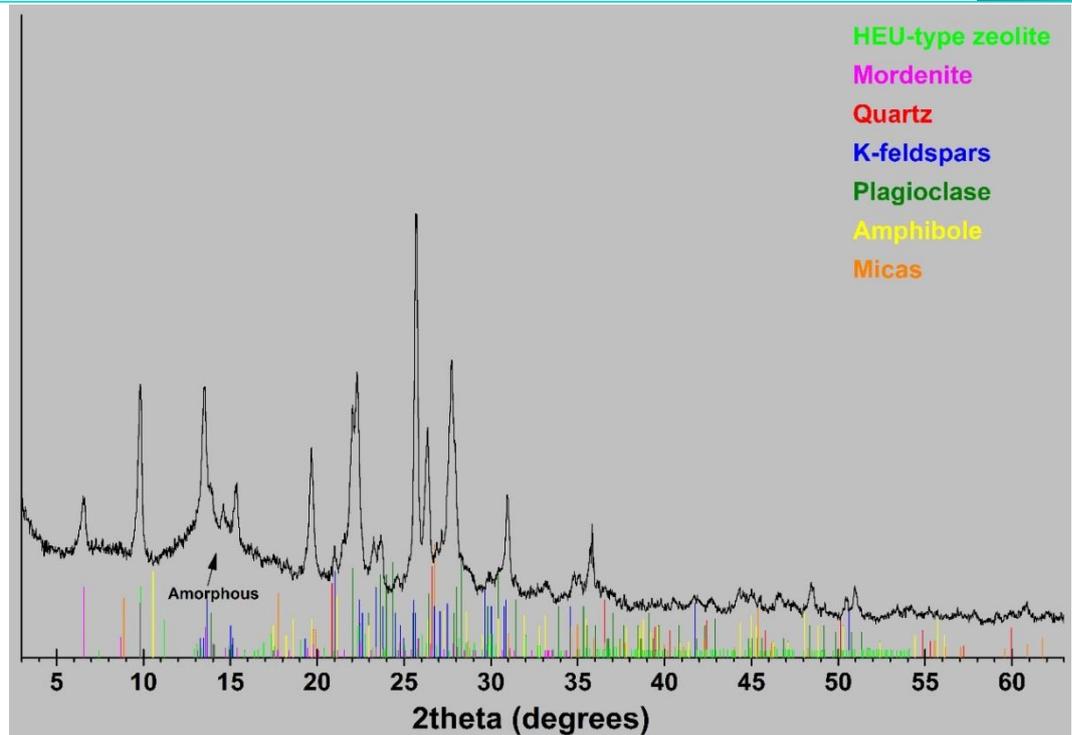
**Fig. 6:** Zeolitic aggregation in sample EVR64, collected from the zeolitized tuffs of Mavri Petra region. Zeolites presenting spherulitic forms, under plane-polarized (a), cross-polarized (b) light and SEM (c and d). Closer observation (d) revealed the co-existence of clinoptilolite (lighter phase) with silica (darker phase).

The rhyolitic sample from Mavri Petra region (EVR59) presents lower alteration grade and the volcanic glass is only locally altered. The mineralogical assemblage is rich, with feldspar as dominant mineral (both plagioclase and sanidine). Sanidine crystals display typical Carlsbad twinning, while plagioclase crystals multiple albite twinning and chemical zoning. Most of the crystals are idiomorphic and no sieve-texture was noticed. Biotite, amphibole and titanite also appear in excellent euhedral crystals. Both biotite and amphibole have strong pleochroism and brown colour. Amphibole twinning and oblique cleavage are typical and distinct. Apatite and zircon can be traced as inclusions within biotite crystals. Observation with SEM indicated high concentrations of Hf in zircon crystals. Moreover, rutile and magnetite of notable dimensions were also detected. SEM analysis indicated the presence of silica phases in all the samples that were identified through XRPD analysis as quartz and cristobalite (Fig. 7).



**Fig. 7:** Photomicrographs and electron backscattered micrographs from sample EVR59, indicating the tabular clinoptilolite crystals (cpt) projected towards a feldspar (fspr) mass, both surrounding a vesicle filling of silica phase (s-ph) formation, probably cristobalite, under plane-polarized (a), cross-polarized (b) light and SEM (c and d).

The XRPD analysis of the twelve (12) representative samples collected from the superficial strata of the volcanoclastic rocks, indicated that all the samples contain clinoptilolite, quartz and feldspars. The average concentration of clinoptilolite is 28 wt%, quartz 15 wt% and K-feldspar 20 wt%. The zeolitic rocks also contain plagioclase, ranging from 5 wt% (EVR22) to 33 wt% (EVR32), which is absent from sample EVR74 collected from Alahopetra region. As shown in Table 2, mordenite was only traced in two samples; EVR71 (Greek-Bulgarian border) and EVR74 (Alahopetra), with concentrations of 3 and 6 wt%, respectively. XRPD analysis revealed the presence of cristobalite in the majority of the samples with concentrations ranging from 1 to 14 wt%, while the sample EVR19 from the old quarries also contains 15 wt% tridymite. The only sample where amphibole was traced through XRPD analysis was sample EVR63 from Mavri Petra region, with its concentration reaching 4 wt%. The average amorphous material of the zeolitic tuffs was calculated 14 wt%.



**Fig. 8:** Representative XRPD pattern of the zeolitized tuffs near the Greek-Bulgarian borders (sample EVR74).

**Table 2.** Semi-quantitative mineralogical composition (wt%) of the zeolitized tuffs of Petrotta region, Evros Prefecture, Greece (Cpt: clinoptilolite, Mor: mordenite, Qtz: quartz, Cris: cristobalite, Trid: tridymite, K-fspr: K-feldspar, Pl: plagioclase, Amph: amphibole, A: amorphous material).

	Cpt	Mor	Mica	Clay	Qtz	Cris	Trid	K-Fspr	Pl	Amph	A
<b>EVR02</b>	35	-	-	-	18	9	-	12	13	-	13
<b>EVR10</b>	22	-	-	-	28	10	-	12	9	-	19
<b>EVR19</b>	33	-	2	-	16	9	15	11	9	-	5
<b>EVR22</b>	23	-	2	1	18	9	-	33	5	-	9
<b>EVR32</b>	35	-	2	1	12	2	-	5	33	-	10
<b>EVR37</b>	33	-	2	2	20	9	-	16	8	-	10
<b>EVR48</b>	35	-	1	-	9	-	-	35	12	-	8
<b>EVR63</b>	30	-	1	-	2	2	-	33	11	4	17
<b>EVR64</b>	30	-	2	2	14	-	-	15	20	-	17
<b>EVR71</b>	6	3	5	-	14	1	-	38	12	-	21
<b>EVR74</b>	15	6	11	-	9	14	-	24	-	-	21
<b>EVR76</b>	38	-	2	3	16	-	-	11	13	-	17

### 3.2. Geochemistry

Chemical analysis of major elements using the X-ray fluorescence (XRF) method has indicated that SiO<sub>2</sub> concentrations range from 67.05 to 71.29 wt%, while Al<sub>2</sub>O<sub>3</sub> from 11.29 to 14.12 wt%, K<sub>2</sub>O from 1.88 to 4.45 wt%, Na<sub>2</sub>O from 0.34 to 3.40 wt% and CaO from 0.95 to 3.21 wt%. The areas around Mavri Petra and the Greek-Bulgarian borders exhibit the highest concentrations in Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>. The tuffs from Mavri Petra also present the highest concentrations in MnO (0.06 wt%) and in P<sub>2</sub>O<sub>5</sub> (0.11 wt%). The highest concentration in MgO (1.02 wt%) is observed in one of the samples collected from Skafida region, but the overall variations are not significant (Table 3).

**Table 3.** Concentrations of major-element oxides (wt%) in the zeolitized rocks of Petrota region, Evros Prefecture, Greece.

	<b>EVR 02</b>	<b>EVR 10</b>	<b>EVR 19</b>	<b>EVR 22</b>	<b>EVR 32</b>	<b>EVR 37</b>	<b>EVR 48</b>	<b>EVR 63</b>	<b>EVR 64</b>	<b>EVR 71</b>	<b>EVR 74</b>	<b>EVR 76</b>
<b>SiO<sub>2</sub></b>	70.53	70.75	70.75	71.29	68.92	69.49	68.06	68.66	67.05	68.35	69.66	68.55
<b>Al<sub>2</sub>O<sub>3</sub></b>	11.65	11.97	11.50	12.38	13.02	12.34	12.18	12.51	13.51	14.12	11.29	12.62
<b>K<sub>2</sub>O</b>	3.51	4.41	3.45	4.21	4.17	4.45	2.98	3.97	3.60	4.11	1.88	2.79
<b>Na<sub>2</sub>O</b>	1.93	1.53	2.49	0.79	3.40	2.13	0.45	2.84	2.16	2.63	1.93	0.34
<b>CaO</b>	1.42	1.18	0.95	2.00	0.96	1.50	3.21	1.32	2.69	2.77	2.80	3.08
<b>Fe<sub>2</sub>O<sub>3</sub></b>	0.91	0.94	0.92	1.14	0.90	0.99	0.91	1.20	2.37	2.63	0.79	1.03
<b>MgO</b>	0.73	0.77	0.42	0.83	0.39	0.45	1.02	0.39	1.00	0.53	0.22	1.00
<b>TiO<sub>2</sub></b>	0.16	0.16	0.17	0.18	0.20	0.17	0.15	0.18	0.29	0.28	0.13	0.16
<b>MnO</b>	0.03	0.02	0.02	0.02	0.03	0.03	0.01	0.02	0.06	0.04	0.04	0.01
<b>P<sub>2</sub>O<sub>5</sub></b>	0.01	0.01	0.01	0.02	0.01	0.02	0.01	0.02	0.11	0.01	0.01	0.03
<b>LOI</b>	9.46	8.40	9.85	7.72	8.08	8.62	11.50	9.03	7.97	5.52	12.18	10.78
<b>Total</b>	100.34	100.14	100.53	100.58	100.08	100.19	100.48	100.14	100.81	100.99	100.93	100.39

Additionally, the results of the 4 Acid digestion ICP-MS analysis, indicated that the overall concentrations for the rare earth elements range for La from 13.5 to 32.8 ppm, for Ce from 27 to 60 ppm, for Y from 8.4 to 19.5 ppm and for Sc from 1 to 4 ppm. The Mavri Petra region, exhibits the highest concentrations in Cu (3.1 ppm), Pb (72.2 ppm), V (32 ppm) and second highest in W (150.4 ppm). The analyzed concentrations of U in two samples of the Palaeokklisi region appear to be 18.9 and 21.8 ppm, relatively high in comparison to the rest that varies from 2.9 to 9.8 ppm. Northwestern of the Palaeokklisi area, close to the Greek-Bulgarian border, the concentrations of Sr appear to be particularly high (872 ppm), compared to 55 to 350 ppm in the other locations, probably because of the proximity to the volcanic centre (Table

4). According to Simov & Bojkov (1992), uranium deposits in southern Bulgaria are related to tectonism and magmatic activation, which could be a possible explanation for the higher concentration of U in the Palaeokklisi region, which is located next to fault.

**Table 4.** Concentrations of trace elements (ppm) in the zeolitized rocks of Petrota region, Evros Prefecture, Greece.

	<b>EVR 02</b>	<b>EVR 10</b>	<b>EVR 19</b>	<b>EVR 22</b>	<b>EVR 32</b>	<b>EVR 37</b>	<b>EVR 48</b>	<b>EVR 63</b>	<b>EVR 64</b>	<b>EVR 71</b>	<b>EVR 74</b>	<b>EVR 76</b>
<b>Li</b>	2.9	4.9	2.4	5.7	4.3	3.9	1.7	3.7	7.3	4.6	2.6	3.8
<b>Rb</b>	205.1	186.9	177.7	179.2	196.6	208.0	140.9	193.5	138.7	143.4	150.7	114.9
<b>Be</b>	5	8	5	8	5	6	7	4	4	4	2	6
<b>Sr</b>	64	55	267	197	92	85	96	101	201	256	350	872
<b>Ba</b>	78	48	90	107	117	84	83	228	591	970	37	279
<b>La</b>	32.8	26.8	27.3	30.4	28.7	25.1	13.5	30.7	24.3	16.2	25.6	26.3
<b>Ce</b>	60	53	53	54	48	47	27	51	49	28	38	50
<b>Th</b>	29.9	28.9	27.8	26.4	29.6	29.5	23.0	30.2	20.8	21.8	19.2	30.4
<b>U</b>	18.9	21.8	7.8	7.2	9.8	7.8	5.7	9.0	6.6	2.9	3.4	6.7
<b>Sc</b>	2	2	2	3	2	3	2	2	4	2	1	2
<b>V</b>	4	6	6	10	7	6	3	9	32	24	2	9
<b>Cr</b>	2	3	3	5	4	3	2	3	10	2	<1	2
<b>Co</b>	11.0	13.5	16.3	15.1	9.7	23.1	13.3	13.9	28.4	28.1	39.3	26.7
<b>Ni</b>	1.5	1.0	1.8	4.7	2.3	2.3	1.2	2.1	4.0	0.8	0.8	1.6
<b>Cu</b>	1.2	1.8	1.5	2.9	1.4	1.2	1.9	1.2	3.1	1.6	1.0	1.8
<b>Zn</b>	41	35	37	51	32	38	25	38	36	31	26	27
<b>Y</b>	16.4	15.7	18.9	19.5	16.3	15.5	9.4	12.3	16.4	8.6	8.4	12.8
<b>Zr</b>	107.1	111.6	104.5	101.4	106.9	104.7	113	98.3	71.4	62.1	96.6	93.8
<b>Nb</b>	23.5	21.2	17.8	21.2	25.8	21.6	24.3	19.9	17.7	14.9	16.2	15.6
<b>Mo</b>	<0.1	0.1	1.2	1.0	1.2	0.7	0.3	0.2	1.2	0.2	0.3	0.1
<b>Ag</b>	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
<b>Cd</b>	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	0.1	<0.1	0.1
<b>Hf</b>	4.0	4.0	3.4	3.7	3.8	3.8	3.8	3.8	2.5	2.1	3.6	3.6
<b>Ta</b>	1.7	1.8	1.7	1.6	1.7	1.7	1.8	1.6	1.3	1.4	1.3	1.3
<b>W</b>	38.2	41.9	38.7	49.8	74.3	93.7	78.5	55.5	150.4	167.4	25.6	31.0
<b>Re</b>	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
<b>In</b>	0.07	<0.05	0.06	<0.05	<0.05	0.08	<0.05	0.05	0.07	<0.05	<0.05	<0.05
<b>Sn</b>	4.4	4.8	4.6	4.6	4.7	4.7	4.6	4.0	2.8	2.1	3.9	3.8
<b>Tl</b>	1.8	1.1	0.8	1.3	2.0	1.7	0.8	1.2	1.0	1.3	1.5	0.9
<b>Pb</b>	72	26.1	15.8	8.2	40.8	35.1	58.1	42.0	72.2	28.1	25.8	30.1
<b>Bi</b>	0.7	0.9	0.6	0.6	0.6	0.8	0.3	0.7	0.5	0.5	0.5	0.5
<b>As</b>	5	4	4	3	5	5	2	2	5	4	4	<1
<b>Sb</b>	0.3	0.3	0.2	0.3	0.2	0.3	0.1	0.1	0.1	0.3	0.1	0.2
<b>Te</b>	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
<b>Se</b>	1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1

#### 4. DISCUSSION

The area of study is affiliated with the Maritsa group volcanoes and more specifically with the Sheinovets caldera, representing the southeasternmost portion of the RM within the borders of Bulgaria, located south of the villages Malko-Gradishte and Mezek (Ivanova *et al.*, 2000; Ivanova, 2005; Yanev and Ivanova, 2010), about 10 km northwest of Petrota village.

Previous studies in the surrounding area suggest that the volcanoclastic rocks were deposited during the Priabonian volcanic phase (Kirov *et al.*, 1990; Filippidis *et al.*, 1995), while more recent studies (Ivanova *et al.*, 2000; Ivanova, 2005; Yanev and Ivanova, 2010) propose a Rupelian age for the acidic formations. Barbieri *et al.* (2000) conducted a geochemical and isotopic study on the zeolite-free rhyolitic rocks of the Petrota region, suggesting that the rhyolitic bodies in the Greek portion of the RM might originate from the eruptive centre of Lozen volcano, northwest of Sheinovets caldera. The detailed data of the study lead to K/Ar radiometric ages of the rocks between  $20.7 \pm 1.6$  and  $24.5 \pm 2.5$  Ma, lower than the age suggested by other researchers. It is also mentioned that the alteration of the rocks occurred approximately 24 Ma ago, after the deposition of the rocks to their final site. Ivanova *et al.* (2001) and Ivanova (2005), based on the K-Ar ages ( $36.71 \pm 1.39$  to  $32.11 \pm 1.28$  Ma) of unaltered rhyolitic bodies from the Sheinovets caldera, suggested the classification of the rhyolitic occurrences into two age groups: a Priabonian in the area of Malko-Gradishte, and a Rupelian in Sheinovets.

Stamatakis *et al.* (1998) suggest that the tuffs cannot be products of air-fall deposits because they overall lack thickness uniformity and the grains in some areas are too coarse to support that theory. Furthermore, the lack of welding and dune-like formations, along with the fact that the tuffs are well-bedded, lead to the conclusion that they could not be originated from pyroclastic surge or flow deposits. Thus, their origin is considered epiclastic and it is proposed that they were formed diagenetically during the Eocene, after the transportation of volcanic ash through water, from the initial site to their current location, in a supra to infra-littoral environment. The tuffs at the time of their deposition were mainly composed of glassy particles, that underwent zeolitization, while the primary minerals remained unaffected. Circulating meteoric water in addition to groundwater, affected the volcanoclastic rocks creating an open hydrological system that favoured zeolitization (Sheppard and Hay, 2001).

According to previous studies (Deffeyes, 1959; Hay, 1966; Hay *et al.*, 1977; Hay, 1978; Surdam and Sheppard; 1978; De' Gennaro and Colella, 1992; Hall, 1998; Hay and Sheppard, 2001; Leggo *et al.*, 2001; Sheppard and Hay, 2001; Ivanova and Gier, 2006), after the eruptive activity, the physiochemical conditions in the area of the volcanic ash deposits are highly acidic and not conducive to zeolitization, as zeolites form in neutral to alkaline environments. Thus,

while the conditions are still acidic, the crystallization of clay minerals is favoured and during that phase, phyllosilicate minerals, like celadonite, form fine aggregations on the glass-shard surface or perimetrically (thin clay-coating). As the environment becomes more alkaline, the formation of zeolite is viable and the volcanic glass shards are altered pseudomorphically into clinoptilolite, leaving a void space in the centre of the shards, where the tabular zeolitic crystals are projected (Fig. 4).

## 5. CONCLUSIONS

The zeolite-rich volcanoclastic rocks in the area of study are highly acidic and their glass shards are partly or fully altered into zeolites. They mainly consist of clinoptilolite, quartz, feldspars (both K-feldspar and plagioclase), cristobalite, biotite and clay minerals, usually celadonite. Muscovite and amphibole, deriving from metamorphic fragments included in the volcanoclastic rocks also participate in small amounts in the mineralogical assemblage. Mordenite and tridymite are rare and only appear locally.

Comparing the mineralogy and geochemistry of similar volcanoclastic formations in the southeastern part of Bulgaria, the zeolitized tuffs of the broader area around Petrota village, are considered to be products of the Rupelian eruptive activity of the Sheinovets caldera. The acidic volcanic ash that was deposited during the Rupelian eruption of the Sheinovets volcano, was transferred to its current location through water. The diagenesis took place probably during the Eocene under open hydrological conditions due to percolating groundwater and meteoric water. The high porosity and permeability of the acidic tuffs permitted the circulation of water in their structure, causing hydrolysis and therefore exchange of cations between the percolating solutions and the tuffaceous formations.

As the conditions were initially highly acidic, the formation of zeolites was not viable until the environment became alkaline. During the acidic phase, argillic alteration is favoured and clay minerals are formed. The clay mineral prevailing during argillic alteration is celadonite.

In the samples with low levels of alteration, the glass shards remain almost unaltered, while fine capillary aggregations of clay minerals formed due to argillic alteration can be found scattered in the groundmass. During that phase the conditions are too acidic for zeolites to form. As the conditions become more conducive to zeolitization, the glass shards are gradually altered to clinoptilolite, forming pseudomorphical structures with distinctive zones.

Although the mineralogical composition of the zeolitized rocks around Petrota village has been the subject of several studies in the past years, further research is required in order to define

the exact physiochemical conditions during deposition and diagenesis, that would provide us with detailed information about the petrogenetic mechanism that took place in the surrounding area.

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