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Mineralogical and Geochemical Study of the Zeolitized Volcaniclastic Rocks of Petrota region, Evros Prefecture, Northeastern Greece

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Introduction

The present study has been carried out to determine the mineralogical and geochemical composition of the zeolitized pyroclastic flow deposits in the Petrota area of Evros prefecture, in northeastern Greece, further to the previous studies that have been conducted in the surrounding area (Kirov *et al.*, 1990; Stamatakis *et al.*, 1996, 1998; Barbieri *et al.*, 2001; Marantos *et al.*, 2006; Filippidis *et al.*, 2016). The broader area is located near the Greek-Bulgarian border and it belongs geotectonically to the eastern Rhodope massif (Kirov *et al.*, 1990; Barbieri *et al.*, 2001). 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 and they were deposited in a supra to infra-littoral environment during the Eocene. Their origin is considered epiclastic and it is suggested that they were transported from their initial to their current location through water. Although most of the zeolite occurrences are characterized as sedimentary type, in rare occasions, due to mixed sulphide and gold mineralization, the zeolite formation is related to hydrothermal alteration (Stamatakis *et al.*, 1996, 1998; Barbieri *et al.*, 2001; Filippidis *et al.*, 2016).

Analytical techniques

In order to determine the mineralogical composition of the zeolite-rich tuffs, 6 thin-polished sections were prepared and studied under a light polarizing microscope and using Scanning Electron Microscopy (SEM) connected to an Energy Dispersive Spectrometer (EDS). The major and trace elements of 12 representative samples were identified by the X-ray fluorescence (XRF) method and 4 Acid digestion ICP-MS analysis, respectively. Furthermore, X-ray powder diffraction (XRD) analysis was performed on 12 randomly oriented powder samples to define the minerals present in the zeolitic tuffs.

Results

Petrographically, most samples present a typical porphyritic texture, containing phenocrysts of primary minerals and metamorphic fragments of different sizes and shapes. Feldspars (sanidine and plagioclase) are the dominant minerals and they appear in phenocrysts with clear zoning and twinning. Although most analytical methods indicate that quartz is abundant in all samples, its presence microscopically isn't represented by phenocrysts. Biotite phenocrysts are abundant and exhibit strong pleochroism with pale to deep brown colour. Amphiboles are observed as primary minerals in the igneous rock, but also as components of the metamorphic fragments. Most amphibole crystals appear brown with intense pleochroism under plane-polarized light. In the sample collected from the Mavri Petra region the amphibole phenocrysts display a distinctive light blue colour. Zeolites can be observed under the microscope mostly in tabular shapes within altered feldspars. As a result of the argillic alteration during zeolitization, clay minerals, such as celadonite, can be found scattered in the altered volcanic groundmass. The mineral assemblage of the metamorphic fragments is dominated by quartz, K-feldspar, plagioclase, micas (muscovite and biotite), amphibole and garnet.

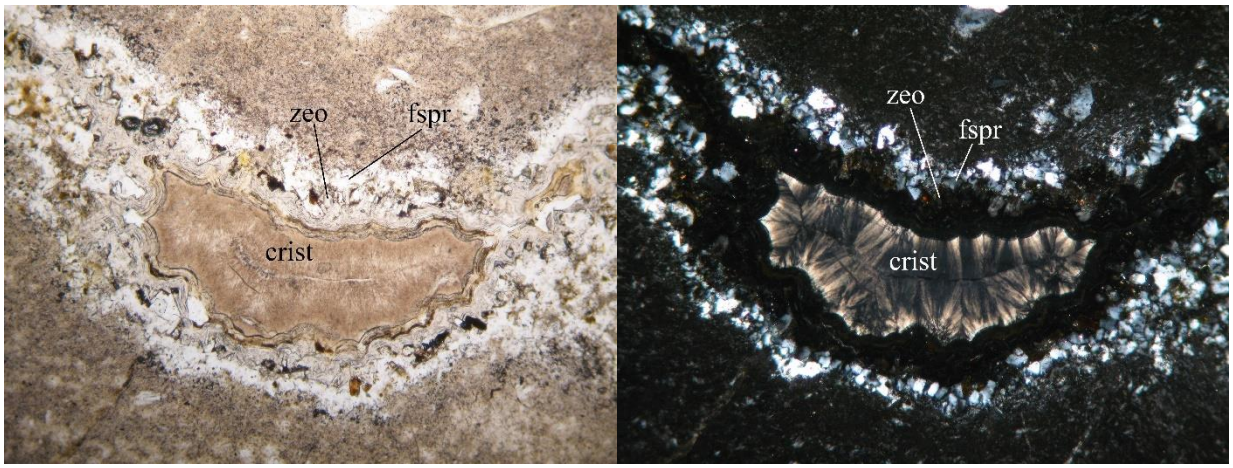

Figure 1. Microphotographs of a cristobalite formation (crist), surrounded by a microcrystalline aggregation of feldspars (fspr) and zeolites (zeo), under plane-polarized (left) and cross polarized light (right) (Mavri Petra region, Evros prefecture).

The mineral phases mentioned above were confirmed by X-ray powder diffraction (XRD). The dominant zeolite in the area of interest is clinoptilolite, while there are some random occurrences of mordenite in small amounts. XRD data also

reveal the presence of quartz, along with its high-temperature polymorph, cristobalite (Fig. 1).

Observation under the Scanning Electron Microscope (SEM) indicates that the dominant minerals are feldspar and zeolite. The groundmass of the investigated samples has undergone diagenetic alteration and zeolites appear as pseudomorphs of plagioclase crystals or as tabular zeolitic aggregations. The glass shards of the porphyritic texture are also partially or fully altered, and cristobalite formations (Fig. 2) appear as a result of the transformation that took place in an open hydrological system (Stamatakis *et al.*, 1998; Kassoli-Fournaraki *et al.*, 2000). Micas are widespread in all the investigated locations, mostly represented by biotite and muscovite. Biotite is observed both in the parental volcanic rock and the metamorphic fragments hosted in it, whilst muscovite is solely a component of the latter. Amphiboles and pyroxenes have also been detected, with amphiboles prevailing in quantity and size (Fig. 2, amp). Additional minerals that have been identified in small amounts are epidote, garnet, titanite, apatite, zircon, ilmenite, magnetite and rutile.

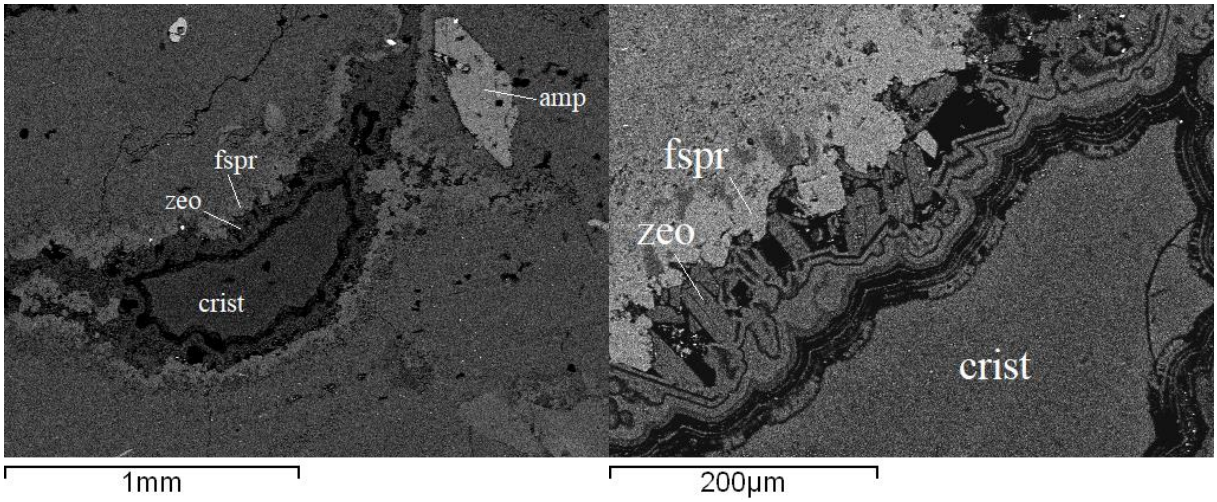

Figure 2. Detailed illustration of the tabular zeolitic crystals (zeo) and the partially altered feldspars (fspr) surrounding the cristobalite formation (crist) of Fig. 1, as displayed under the Scanning Electron Microscope (SEM).

Chemical analysis of major elements using the X-ray fluorescence (XRF) method has indicated that SiO_2 concentrations range from 67,05 to 71,29 wt%, while Al_2O_3 from 11,29 to 14,12 wt% and K_2O from 1,88 to 4,45 wt%. The rest of the elements appear in minor amounts.

Additionally, 12 representative samples of the same area were analyzed through 4 Acid digestion ICP-MS method in order to define the concentrations of 45 trace elements, including some rare earth elements (La, Ce, Y, Nb, Sc). The overall concentrations for La range from 13.5 to 32.8 ppm, for Ce from 27 to 60 ppm, for Y from 8.4 to 19.5 ppm, for Nb from 14.9 to 25.8 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), Mn (476 ppm), V (32 ppm), P (0.048 %) 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 vary from 2.9 to 9.8 ppm. Northwestern of the Palaeokklisi area, close to the Greek-Bulgarian boarder, the concentrations of Sr appear to be high (872 ppm) compared to 55 to 350 ppm in the other locations.

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