Zeolitized volcaniclastics from northern part of Dzhebel depression, E. Rhodopes: stratigraphy, petrography and mineralogy

Зеолитизирани вулканокластити от северната част на Джебелската депресия, И. Родопи: стратиграфия, петрографска и минераложка характеристика

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Key words: Eastern Rhodopes, Paleogene, acid volcaniclastics, glass alteration, clinoptilolite.

Dzhebel depression is an Oligocene structure developed in the SW parts of Eastern Rhodopes, filled by volcaniclastic and sedimentary rocks. The volcaniclastics are represented by the explosive products of the 1st acid, 2nd intermediate and 2nd acid Rupelian phases of the Paleogene Eastern Rhodopean volcanism. They lie on Rupelian sandstones and conglomerates and are covered by the sandstones of Dzhebel formation (Atanasov, Goranov, 1975). This study deals with the pyro- and epiclastic rocks, erupted during the 2nd acid phase occupying an area of ~2×8 km to the west of the town of Momchilgrad. The field works revealed that the eruptive stratigraphy of this succession is similar to the contemporaneous section of Belia Bair – Zhelezni Vrata zeolite deposits (Yanev et al., 2006). Knowing that they are also zeolitized (Djourova, Aleksiev, 1989) we have started a thorough study of the section exposed near Plazishte village (Ivanova et al., 2010). Along with studying the distribution, abundance and chemistry of secondary mineral association, many data on the nature of the precursor volcaniclastics were collected allowing source area to be inferred and its eruptive history to be, at least, partly reconstructed.

The section studied comprises (from bottom to top) three massive pyroclastic flow deposits covered by a stratified unit of submarine flow, fall-out and epiclastic beds and is respectively divided into two informal lithostratigraphic units: lower ignimbrite packet and upper mixed one.

The first ignimbrite (>10 m thick) is dominated by ash-sized shards. Pumice is more abundant in the lowermost levels. Dense rhyolite lava and crystal fragments are rare. Fragments of carbonized trees were found, indicating subaerial eruption. A very powerful explosion can cause the observed high degree of magma fragmentation. During such events the vent erodes and gets wider, resulting in less energetic eruptions and lower degree of fragmentation (Fisher, Schmincke, 1984). Respectively, the middle ignimbrite (8–10 m thick) is coarser and pumice dominated. Pumice fragments are ash to lapilli in size as these in the middle parts of the unit are flattened and cracked. Rhyolite lava fragments, single latite xenoliths and fine ash-sized shards are also present. The association of crystals is richer that in the first ignimbrite. The third ignimbrite (10–12 m thick) is more variable. The lower parts are massive; build up by ash to fine lapilli in size pumice fragments. Fine lava clasts and crystal fragments are present in small quantity. The crystal content increases upward so as the upper parts represent an alternation of crystal- and pumice-dominated but still crystal-rich levels. This ignimbrite was probably derived from deeper crystal-rich parts of the chamber (confirmed by the amphibole geobarometry). Normal grading of pumice clasts and their abundance in the lower parts of the ignimbrites studied are thought to indicate submarine deposition of still hot flows.

The association of pyrogenic minerals is richest in the upper two flows and includes quartz, plagioclase, sanidine ($Or_{42–69.5}$) to Na-sanidine ($Or_{45–70}$), biotite, Mg-hornblende (Si 7.04–7.4 *apfu*, Mg# 68–74), diopside ($Wo_{47.3}En_{39.2}$, Mg# 78), and accessories (apatite, titanite, magnetite). Plagioclase is sometimes zonal with more basic rim (core $An_{19.5}Or_{7.1}$, rim $An_{18.5–33}Or_{7.5–3.4}$) and sieve-textured (core $An_{49.2}Or_{3.8}$, rim $An_{46}Or_{9.3}$) that could indicate magma mixing with rising from depth more basic magma batches. Amphibole composition was used to calculate (Ridolfi et al., 2010) the parameters during its crystallization (temperature 737–813±22 °C; pressure 53–105 MPa corresponding to 2–4 km depths; 3.6–4.1±0.4% H_2O).

The source area is unknown but a candidate lies just to the NE of the area studied – Dambalak volcano, where acid lava and volcaniclastic rocks crop out in its basal parts (Byuyukdere; Yordanov et al., 2008 and the references therein), covered by younger latite lava and volcaniclastic rocks. This assumption coincides with the grain size distribution and variations in thickness of the studied 2nd acid phase volcaniclastics, all getting thicker towards Dambalak volcano.

The upper mixed packet (25–30 m thick) encloses different in origin volcaniclastic varieties: extremely fine-grained ash-fall deposits, one thin pumice flow unit, silty (with marine fossils) to sandy crystal-rich epiclastics, probably laid by cold water-supported flows. Only the fall-out tuffs seem not consistent with the inferred proximity to the source so they can be interpreted as distal facies of another vent area.

All of the glass particles, in both pyro- and epiclastic varieties throughout the whole section, are completely replaced by clinoptilolite, feldspars, phyllosilicates, and opal–CT. Clinoptilolite content (according to Rietveld refinement) varies from <20% in the carbonate-containing epiclastics to over 80% in the crystal-poor ignimbrites. In the crystal-rich epiclastics the quantity of clinoptilolite is 40–50%.

Although no fresh glass was observed, its chemistry was obtained by analyzing one glass inclusion in a quartz crystal. When compared with the composition of the whole rocks we can conclude that during glass alteration SiO_2 does not change significantly and Al_2O_3 tends to concentrate in the altered rocks. A part of K_2O seems leached from the ignimbrites while its content increases in the finest fall-out tuffs. Na_2O is more efficiently removed from the topmost and lowermost parts of the section. CaO, Fe_2O_3, TiO_2 and especially MgO tend to enrich in the products of alteration (particularly in clays).

Clinoptilolite forms fine prismatic or plate-lake crystals (up to 30–50 μm) replacing both shards and pumice lithics or is dispersed in the matrix. Regarding the exchangeable cation content, clinoptilolite is quite variable throughout the section, especially within the lower packet. It is Ca–K in the base of all three ignimbrites from the lower packet, Na–K–Ca in the upper parts of the lower two flow units and Ca–K–Na in the upper parts of the 3rd ignimbrite. Clinoptilolite composition is more stable in the upper mixed packet (Ca–K) and is relatively enriched in Mg. The Si/Al ratio varies from 4.63 to 5.55 (Ivanova et al., 2010).

Authigenic feldspars are present in all of the samples. According to their composition two types of feldspar were found: pure adularia (to $Or_{92.3}$) with platy to typical pseudorhombic crystals (up to 7 μm), present in most of the samples, and K- to Na-sanidine ($Or_{92.3–42}An_{0.6–7}$), found in the fall-out tuffs only. The last variety appears as small grains (<10 μm) with irregular shape, scattered in the matrix.

Phyllosilicates appear as delicate aggregates coating the original surface of glassy particles, regularly distributed in the matrix and in the central hollows of already zeolitized shards. In composition they are relatively poor in Al and enriched in Fe and K indicating abundance of unexpandable mica layers.

Opal–CT phases are always present. Traces of *fibrous zeolite* phase (mordenite?) and hexagonal or rounded prismatic crystals of authigenic *apatite* (up to 20 μm), were observed by SEM. We were unable to analyze the apatite observed, but only fluorapatite has been identified so far in other phosphorite occurrences (Stoilov et al., 2006), hosted by Rupelian pyroclastics in Eastern Rhodopes.

The alteration of the 2nd phase acid volcaniclastics from the northern parts of Dzhebel depression fit to the model proposed to explain the zeolitization of large volumes of acid volcaniclastics in Eastern Rhodopes (Yanev et al., 2006 and references therein): regional low-temperature hydrothermal system operating in shallow marine environment. Relatively higher depositional temperatures of the pyroclastic flow deposits enhanced the processes of the initial glass hydration and dissolution. Marine waters also contributed to the process being the pore fluid providing cations (like Mg^{2+}) and water molecules for the newly forming phases.

References

Atanasov, G., A. Goranov. 1975. Paleogeography and sediment formation during the Paleogene in the East Rhodope Mountain. – *Geologica Balc.*, *5*, 1, 73–86.

Djourova, E., B. Aleksiev. 1989. Zeolitic rocks in the East Rhodope Paleogene depression. – *Geologica Rhodopica, 1*, 240–245.

Fisher, R. V., H.–U. Schminke. 1984. *Pyroclastic Rocks*. Heidelberg, Springer–Verlag, 472 p.

Ivanova, R., Y. Yanev, E. Vasilieva, L. Machiels, J. Elsen. 2010. Zeolitization of acid pyroclastic deposits from northern parts of Dzhebel depression, E. Rhodopes, S. Bulgaria. – In: *Book of Abstracts of the 8-th Intern. Conf. on the Occurrence, Properties and Utilization of Natural Zeolites "Zeolite 2010"*. Sofia, 117–118.

Ridolfi, F., A. Renzulli, M. Puerini. 2010. Stability and chemical equilibrium of amphibole in calc-alkaline magmas: an overview, new thermobarometric formulations and application to subduction-related volcanoes. – *Contr. to Mineral. and Petrol.*, *160*, 45–66.

Stoilov, V., I. Donchev, O. Petrov, V. Petkova, Y. Kalvachev, N. Lihareva. 2006. Mineral composition and comparative characteristics of Bulgarian Oligocene phosphorites. – *Rev. Bulg. Geol. Soc.*, *67*, 1–3, 143–148.

Yanev, Y., J.–J. Cochemé, R. Ivanova, O. Grauby, E. Burlet, R. Pravchanska. 2006. Zeolites and zeolitization of acid pyroclastic rocks from paroxysmal Paleogene volcanism, Eastern Rhodopes, Bulgaria. – *N. Jb. Miner. Abh.*, *182*, 3, 265–283.

Yordanov, B., S. Sarov, S. Georgiev, V. Valkov, E. Balkanska, V. Grozdev, N. Markov, R. Marinova. 2008. *Explanatory Note to the Geological Map of the Repiblic of Bulgaria in Scale 1:50 000. Map Sheet Kardzhali.* Sofia, Ministry of Environment and Water. Bulgarian National Geological Survey, 130 p.