Mineral chemistry of the collision-related acid Paleogene volcanic rocks of the Eastern Rhodopes, Bulgaria

Химизъм на скалообразуващите минерали на палеогенските колизионни кисели вулканити в Източните Родопи

***Yotzo Yanev*[1], *Rositsa Ivanova*[2]**
***Йоцо Янев*[1], *Росица Иванова*[2]**

[1] Bulgarian Geological Society; E-mail: yotzo_yanev@yahoo.com
[2] Geological Institute, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria; E-mail: rossiv@geology.bas.bg

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It is already well-known that the Paleogene collision-related volcanism in the Eastern Rhodopes is bimodal in composition, as the two compositional members have intermediate (rarely to basic) and acid composition; the last being represented by rhyolite, trachyrhyolite, rhyodacite, trachyrhyodacite, rarely trachyte and trachydacite. Many papers deal with the individual occurrences of the acidic volcanics in the area, others report general views on different geodynamic, geological, petrological and volcanological problems. Such a review of the acid volcanism and its products in the Eastern Rhodopes is made by Yanev (1998). Nevertheless, the chemistry of the rock-forming minerals, regarding especially the acid members, has been often out the scope of the papers. We focus our attention on the chemistry of mineral associations found in the acid volcanics, as a set of 550 microprobe (WDS and EDS) analyses is the basis of our study. Despite having quite poor phenocryst assemblages (quartz, sanidine, plagioclase, biotite, rarely amphibole and/or clinopyroxene as well as Fe-Ti oxides) the chemistry of the mafic phenocrysts is variable and that allows studying the processes of isomorphic substitution in them. Phenocrysts assemblages provide information about the conditions during magma crystallization in the crust. The composition of the feldspars indicates presence of mixing (and/or mingling) processes.

Clinopyroxenes are quite rare and vary in composition from diopside to augite (in the products of the earlier stages in Borovitsa caldera and Arda group volcanics) and to hedenbergite (in Tatarevo). All these varieties are poor in Al, but tetrahedral deficiency rarely occurs. The species having ^{VI}Al (from Borovitsa and Madzharovo) contain small quantities of tschermakite and jadeite molecules that are typical high-pressure components. Na enters the clinopyroxene structure mainly as acmite molecule, resulting in a positive correlation between Na and Fe^{3+}, and rarely as jadeite one. Ti content is low, correlating positively with Al and negatively with Si. This reflects the most important non-quadrilateral substitution in pyroxenes (Ti+2Al↔Mg+2Si).

Amphiboles are more common than pyroxenes and according to their composition they are mainly Mg-hornblende and Mg-edenite, rarely pargasite and Mg-hastingsite. All they show higher alkaline and ^{IV}Al contents reflecting the transitional alkaline character of the Eastern Rhodopes volcanics. The main substitutions in Ca-amphiboles are edenite and tschermakite (Leake, 1965): $^{IV}Al+(Na+K)_A \leftrightarrow \square$, Si and $Si+R^{2+} \leftrightarrow {}^{IV}Al+{}^{VI}Al$, respectively, as the first is better represented in the Eastern Rhodopes. Ti content is relatively low. In some cases it correlates positively with the crystallization temperature and negatively with the oxygen fugacity. A clear positive correlation with ^{IV}Al is observed in other cases. It is caused by the following variety of tschermakite substitution: $Ti+2{}^{IV}Al \rightarrow Mg+2Si$.

Biotite is the most common mafic phenocryst, presents in all varieties of the acid volcanics occurring in the Eastern Rhodopes. It is Mg-rich annite (Mg# between 0.5 and 0.67) as ^{IV}Al varies widely from 1.67 to 2.67 *apfu*. The clear negative correlation between Mg# and ^{IV}Al results from the most important substitution in biotite $(Mg, Fe)+Si \leftrightarrow 2{}^{IV}Al$. The octahedral Al is low: up to 0.2 *apfu*. A negative correlation between ^{IV}Al and ^{VI}Al, which can be explained by the same substitution scheme, is observed in the biotite in the Borovitsa volcanics. Ti content varies between 0.3 and 0.67 *apfu* (the last in Hisar volcano). A negative correlation between Ti and Mg# is observed in some of the Borovitsa volcanics, as well as in some of the volcanoes in Momchilgrad–Arda region. This correlation is due to the substitution Ti+2Al↔Mg, Fe+2Si, which is an extended version of the scheme above. From the possible volatile components in biotite, only F content is measured in some of the volcanoes. In the southern region its content clearly increase from oldest

(Priabonian) toward the youngest Rupelian phase: the average F content in biotite from the Priabonian phase is 0.14–0.29 wt.%, in the products of the II Rupelian phase is 0.28–0.68 wt.%, in the products of the III phase is 0.48 wt.%, in the products of the IV phase (Zli Vrah volcano) up to 1.34 wt.%.

Feldspars are plagioclases (varying from labradorite to acid oligoclase) and sanidine. The last is absent only from the phenocryst assemblage of the Hisar volcano lavas, which are the most basic (trachydacite). Anorthoclase is present as single subphenocrysts, microlites or coating on sanidine crystals. Plagioclases normally show weak compositional variation (excepting these from Sheinovets caldera, Ivanova, 2006) as do some sanidine due to the range in its Ba content (e.g. in the Borovitsa caldera ignimbrites). In the central zones of these crystal clasts BaO reaches 8.9 wt.% ($Cn_{17.1}$).

Basic plagioclases were identified in some of the studied volcanics (Sheinovets caldera, Sveta Marina volcano, Borovitsa caldera domes) together with the acidic plagioclases typical of acid volcanic rocks. The basic plagioclases appear as strongly corroded cores in more acid crystals (in Shenovets); but also as phenocrysts with sieve-texture (as in the other two regions) indicating mixing process between acid (rhyolitic) and more basic (probably latitic) melts.

Oxide minerals, together with apatite, zircon and titanite, are the main accessory phases in the acid rocks in the Eastern Rhodopes. The oxide minerals in the non-oxidized perlite glasses (black, gray, and white) have only been analyzed. These are oxides of Ti and Fe^{2+} (ferropseudobrookite to ilmenite) and of Ti, Fe^{2+} and Fe^{3+} as the last form an almost continuous row from Ti-magnetite to magnetite–hematite (ratio of Fe^{2+}:Fe^{3+} up to 0.33).

Our estimations of *temperature, pressure, oxidation potential and water contents* of the magma during crystallization of the mafic phenocrysts are based on amphibole chemistry following the calculation schema of Ridolfi et al. (2010), combined with data from the three-feldspar geothermometer. The temperatures obtained from Borovitsa volcanics indicate decreasing temperatures toward later stages of the caldera volcanism, unlike most of the caldera systems. The same was previously proposed on the basis on the phenocryst chemistry and was explained by magma drainage from increasingly higher levels of the magma chamber, resulting in a homodrome trend of evolution of the caldera volcanics (Yanev, 1998). Regarding the volcanics from the Momchilgrad–Arda region, it was confirmed that the pyroxene-containing lava rocks are formed at higher temperature than amphibole-containing ones (Yanev, 1998).

Based on the exponential dependence of Al in amphibole on pressure (Ridolfi et al., 2010), the last was calculated and values of 0.64–1.16 kbar were obtained for the lavas in the Borovitsa caldera. These amphiboles crystallized in crustal conditions, close to the surface, from 2.4 to 4.4 km, respectively. Low to middle values were obtained for the pressure during amphibole growth in the magma of Sheinovets caldera (0.84–1.65 kbar corresponding to depths of 3.2–6.2 km); middle values for the Lozen volcanics (1.02–1.19 kbar and depths 3.9–4.5 km); and high values for Studen Kladenets volcano (2.97 kbar, 11.2 km depth). The obtained values for the oxygen fugacity lie between HM and NNO buffers, closer to the second one (ΔNNO 0.13–2.3). All studied rocks are similar to other high-K Ca-alkaline and transitional acid volcanics from the “orogenic belts”.

According to the amphibole geohygrometer of Ridolfi et al. (2010), water contents of the Borovitsa caldera magmas increase from the second stage lavas (2.61–3.93%) to the last stage domes (3.69–4.01%), whereas the explosivity decrease. The water content of the lavas from the Momchilgrad–Arda region is higher: 4.12–6.21% in Sheinovets and Lozen, and 6.82% in Studen Kladenets. All volcanics having higher water contents are accompanied by large volumes of perlites as their water content correspond well to the values calculated using the amphibole chemistry.

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