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

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Abstract. The paper is based on more than 550 microprobe (both WDS and EDS) analyses of clinopyroxenes, amphiboles, biotite, feldspars and accessory oxides from the Borovitsa (BR) and Momchilgrad–Arda (MAR) volcanic regions of the Eastern Rhodopes.

Clinopyroxenes are rare and vary from diopside to Fe-augite. They are poor in Al, but tetrahedral deficiency rarely occurs. Na enters the pyroxene structure mainly as acmite molecule, resulting in a positive Na–Fe^{3+} correlation, and rarely as jadeite one. Ti contents are low, correlating positively with Al and negatively with Si that reflects the $TiAl_2 \leftrightarrow MgSi_2$ substitution.

Ca-amphiboles are more common. They are mainly Mg-hornblende and Mg-edenite, rarely pargasite and Mg-hastingsite. The main substitutions are of edenite and rarely of tschermakite type. Ti content is relatively low, sometimes correlating positively with the temperature and negatively with the fO_2. A positive Ti–^{IV}Al correlation is observed in other cases, caused by Ti+2^{IV}Al→Mg+2Si substitution.

Biotite is presented in all studied volcanics. It is Mg-rich annite ($Mg^{\#}$ 0.53–0.67). The observed negative ^{IV}Al–$Mg^{\#}$ correlation results from the $(Mg, Fe)O + SiO_2 \leftrightarrow Al_2O_3$ substitution. The ^{VI}Al is low: up to 0.2–0.3 *apfu*. A negative ^{VI}Al–^{IV}Al correlation, explained by the same substitution scheme, is observed in the BR biotites. Ti contents are 0.3–0.7 *apfu*. A negative Ti–$Mg^{\#}$ correlation is found in some volcanics due to the substitution Ti+2Al↔Mg, Fe+2Si. The F contents in the biotites from MAR increase from the oldest (Priabonian) towards the youngest Rupelian phase.

Feldspars are plagioclase, sanidine and rare anorthoclase. The plagioclases are weakly zoned. Some sanidines have rich in Ba central zones or rims (up to 8.9 wt.% or $Cn_{17.1}$). Basic, strongly corroded plagioclases (up to labradorite or bytownite) were identified in some of the volcanics together with the acidic ones (oligoclase to andesine), indicating mixing process between rhyolitic, and probably latitic melts.

Oxide minerals, together with apatite, zircon and titanite, are accessories. The first ones are Ti–Fe^{2+} (ferropseudobrookite to ilmenite) and of Ti–Fe^{2+}–Fe^{3+} oxides as the lasts form a continuous row from Ti-magnetite to magnetite–hematite.

The temperatures (according to amphibole and feldspar chemistry) for BR decrease towards the later stages of the caldera volcanism. In MAR was confirmed that the pyroxene-bearing rocks were formed at higher temperature than amphibole-containing ones. Based on the exponential dependence of Al in amphibole vs. pressure, the values of 0.64–1.16 kbar have been obtained for BR volcanics (corresponding to the 2.4–4.4 km depth) and of 0.84–2.97 kbar for MAR (corresponding to the 3.2–11.2 km) The fO_2 lies between HM and NNO buffer, close to the second one (ΔNNO 0.13–2.06). According to the amphibole geohygrometer, water contents of the Borovitsa caldera magmas increase from the lavas of the 1st (2.61–3.92%) to the last stage (3.69–4.01%), whereas the explosivity decreases. The water contents of the Momchilgrad–Arda region lavas are higher (4.12–6.82%). All water rich lavas have formed perlites and their water contents, in most of the cases, correspond to the values calculated using the amphibole chemistry.

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Йоцо Янев, Росица Иванова. Химизъм на скалообразуващите минерали на палеогенските колизионни кисели вулканити в Източните Родопи

Резюме. Статията обобщава резултатите от 550 микросондови (WDS и EDS) анализи на пироксени, амфиболи, биотит, фелдшпати и акцесорните оксиди в Боровишкия (БР) и Момчилград–Ардински (МАР) район.

Клинопироксените се срещат рядко и по състав варират от диопсид до Fe-авгит. Те са бедни на Al, но тетраедричен дефицит се проявява рядко. Na влиза в пироксеновата структура рядко като жадеитова, а най-често като акмитова молекула, което води до поява на положителна Na–Fe^{3+} корелация. Съдържанието на Ti е ниско, корелирайки положително с Al и отрицателно със Si, което се дължи на субституцията TiAl$_2$↔MgSi$_2$.

Ca-амфиболи се срещат по-често. Те са главно Mg-хорнбленда и Mg-еденит, рядко паргасит и Mg-хейстингсит. Главната субституция в тях е от еденитов тип, по-рядко от чермакитов. Ti съдържание е сравнително ниско, корелиращо положително в някой от вулканитите с температурата и отрицателно – с fO$_2$. В други Ti положително корелира с ^{IV}Al, което се дължи на субституцията Ti+2^{IV}Al→Mg+2Si.

Биотитът е представен повсеместно. По състав е богат на Mg анит (Mg$^{\#}$ 0,53–0,67). Наблюдаваната негативна ^{IV}Al–Mg$^{\#}$ корелация се дължи на субституцията (Mg,Fe)O+SiO$_2$↔Al$_2$O$_3$. Количеството на ^{VI}Al е ниско – до 0,2–0,3 *apfu*. Със същата схема на заместване се обяснява и отрицателната ^{VI}Al–^{IV}Al корелация, наблюдавана в биотитите на БР. Ti съдържание е между 0,3 и 0,7 *apfu*. Наблюдава се отрицателна Ti–Mg$^{\#}$ корелация, дължаща се на заместване по схемата Ti+2Al↔Mg,Fe+2Si. В МАР съдържанието на F се увеличава от най-старата, приабонска към най-младата рупелска фаза.

Фелдшпатите са представени от плагиоклаз, санидин, рядко и анортоклаз. Плагиоклазите най-често са слабо зонални. Някои санидини имат високо Ba съдържание в централните или периферните зони (до 8,9 wt.% или Cn$_{17.1}$). В някои от вулканитите присъстват силно кородирани базични плагиоклази (до лабрадор или битовнит), заедно с кисели такива (олигоклаз–андезин), което е указание за миксинг на риолитова, вероятно с латитова магма.

Оксидните минерали, заедно с апатита, циркона и титанита са акцесорните фази. Установени са Ti–Fe^{2+} (феропсевдобрукит до илменит) и Ti–Fe^{2+}–Fe^{3+} оксиди, образуващи непрекъсната редица между Ti-магнетит и магнетит–хематит .

Според състава на амфибола и фелдшпатите температурата на кристализация в БР намалява към по-късните стадии на калдерния вулканизъм. В МАР се потвърди, че пироксенсъдържащите вулканити имат по-висока температура от амфиболсъдържащите. Въз основа на експоненциалната зависимост на налягането от съдържанието на Al в амфиболите за БР беше получено налягане от 0,64–1,16 kbar (отговарящо на дълбочина 2,4–4,4 km), а за МАР – 0.84–2.97 kbar (отговарящо на дълбочина 3.2–11.2 km). fO$_2$ е между НМ и NNO буфер, по-близка до втория (ΔNNO=0,13–2,06). Според амфиболовия геохигрометър водното съдържание на БР се увеличава от началните фази (2.61–3.92%) до последната (3,69–4,01%), докато експлозивността им намалява. В МАР съдържанието на вода е по-високо (4,12–6,82%). Всички богати на вода лави са образували перлити като съдържанието на вода в тях в повечето от случаите отговаря на изчисленото с амфиболовия геохигрометър.

Introduction

The volcanic activity in the Eastern Rhodopes resulted from the collision between the north-ward-advancing parts of the African plate and the active continental edge of Eurasia that took place in Paleogene (Yanev & Bahneva 1980; Dabovski et al. 1991; Yanev 2003a). It is cyclic in character (4 intermediate phases alternate with 5 acidic: one Priabonian and 3 or 4

Rupelian, respectively) and bimodal in composition as almost equal volumes of intermediate and acid volcanics were produced (Ivanov 1960, 1963), together with a little basic varieties. Many papers are known to deal with the individual occurrences of the Paleogene volcanics in the Eastern Rhodopes; others report general views on different geodynamic, geological, petrological and volcanological problems and the most recent ones are collected in a special volume of Acta Vulcanologica, devoted on the Rhodopes (cited in Yanev 1998). Nevertheless, the chemistry of the rock-forming minerals, regarding especially the acid members of this volcanism, has been often out the scope of the papers, excepting some works like the description of the Golobradovo perlite deposit (Yanev 2003b), the study of Sheinovets caldera volcanics (Ivanova 2006) and others. A summary on the acid volcanics in the area was made by Yanev (1998). The microprobe dataset (over 550 analyses), cited here and after as Appendix (not printed, but deposited as file appendix_yanev2010 on the web page) on the chemistry of phenocrysts, present in the acid volcanics, accumulated during the last decades, gives us a tool for better understanding of the evolution of rock-forming mineral associations, both in individual volcanoes and volcanic regions, composing the picture of one case of collision-related volcanic area.

Despite observing quite poor phenocryst associations in the acid volcanics (quartz, plagioclase, sanidine, biotite, in some varieties amphibole and/or clinopyroxene, as well as Fe–Ti oxides), the composition of mafic minerals is notably diverse that allows studying the schemes of their isomorphic substitutions. The feldspars permitted us to identify mixing (and/or mingling) phenomena in some of the acid rocks. All phenocrysts together gave information on the conditions of the magma crystallization. The groundmass (felsitic, spherulitic, perlitic and granoblastic in subvolcanic bodies) has not been studied here.

Brief description of the studied Paleogene acid volcanics

Three Paleogene volcanic regions were distinguished in the Eastern Rhodopes and two of them are discussed here (Fig. 1) – northwestern, Borovitsa (BR) and southeastern, Momchilgrad–Arda (MAR) (Ivanov 1960). A brief description of the acid volcanics in these regions is presented here just to give an idea of their position in the evolution of the Eastern Rhodopes. Their chemistry is discussed in detail in Yanev (1998) and some other papers listed in the references. Only volcanic edifices and domes that are objects of this study are described below.

BR is dominated by a large caldera of the same name, so two groups of volcanics were distinguished in respect to it: intra- and extra-caldera. Six main stages were identified in the tectonomagmatic evolution of Borvitsa caldera (Yanev 1990; Yanev et al. 2005; Dhont et al. 2008):

- 1st stage. Deposition of crystal-rich ignimbrite units containing zonal plagioclase (labradorite–oligoclase), Ba-rich zonal sanidine, biotite, diopside, rarely quartz subphenocrysts. The ignimbrites (33.5 Ma[1]) are trachyte to trachyrhyodacite in composition, strongly welded in the western parts of the caldera and not welded in the eastern.

- 2nd stage. The fast eruption of vast amount of pyroclastic material led to formation of nested caldera complex. The central Murga caldera (Yanev 1990) has a diameter of 7–10 km. Crosscutting ring body of ignimbrite-like trachyrhyodacite to rhyolite were emplaced within its bounding faults. The phenocrysts are quartz, sanidine, oligoclase, biotite, rarely amphibole and diopside as some of the feldspars and mafic minerals are altered. The groundmass is heterogeneous, composed by fiamme-like lenses, altered to quartz–albite aggregate, enclosed in matrix of adularized

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[1] All ages in the paper are K–Ar, obtained by P. Lilov on bulk samples. They are cited in Yanev (1990) and Lilov et al. (1987)
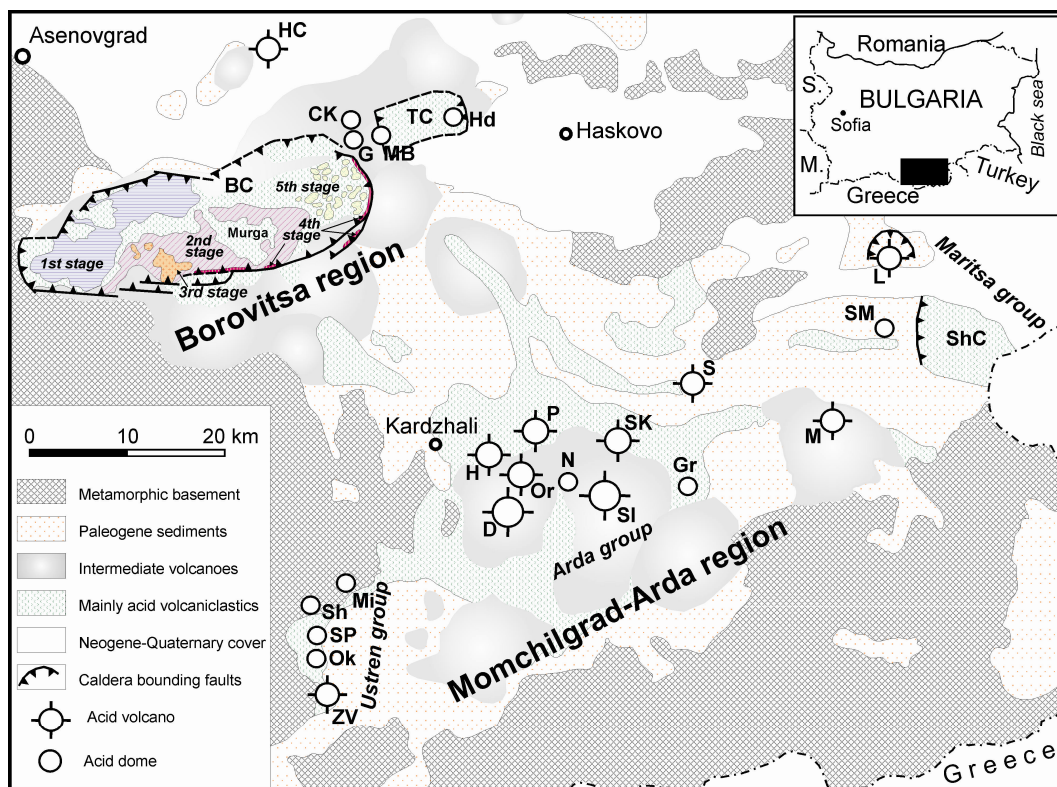
Fig. 1. Location map of the studied acid volcanoes and dome areas in the Eastern Rhodopes. *Calderas*: (ShC) Sheinovets; (TC) Tatarevo (according to Yordanov et al. 2008b); (BC) Borovitsa (with the stages of formation); *volcanoes*: (L) Lozen; (M) Madzharovo; (S) Silen; (SK) Studen Kladenets; (SI) Sveti Iliya and (D) Dambalak composite volcanoes; (P) Perperek; (Or) Ormanlar; (H) Hisar; (ZV) Zli Vrah; (HC) Haykanska Chuka; *domes*: (SM) Sveta Marina; (Gr) Gerena; (N) Nanovitsa; (Mi) Mishevsko; (Sh) Shterna; (SP) Schupenata Planina; (Ok) Ortakaya; (Hd) Hisar (in Tatarevo caldera), (MB) Mineralni Bani, (CK) Cherniya Kamak, (G) Gradishte

shards (<1 mm). They were cut by numerous bodies of black, partly zeolitized perlite, containing the same, but not altered phenocrysts.

• 3rd stage. Eruption and depositions of pyroclastic material. The western parts of the ring body were intruded by a subvolcanic stock (33 Ma) of trachydacite to trachyrhyolite with phenocrysts of quartz, sanidine, zonal plagioclase (andesine to oligoclase) and biotite.

• 4th stage. The large eruptions resulted in a new caldera subsidence and formation of Borovitsa caldera in its present-day shape and size (15×30 km). Few dykes (32.5 Ma) and one

small body were emplaced in its bounding faults with trachydacite to rhyolite composition. They contain quartz, sanidine, oligoclase, biotite, amphibole and/or diopside.

• 5th stage. Several tens of high-Si trachy-rhyolite domes and cryptodomes with perlitic peripheries (30–32 Ma) were emplaced on or very close to the surface. They contain rare phenocrysts of quartz, zonal sanidine (regarding its Ba contents), sometimes coated by anorthoclase, zonal plagioclase, biotite and amphibole (together with diopside in one dome). This stage ended with intrusion of very

rich in phenocrysts (>50%) trachyrhyolite (building Letnitsa dome) being the residue of a zonal magma chamber (Hildreth 2004).

- 6th stage. Both the caldera fill and frame were cut by dyke swarms with composition varying from shoshonite to rhyolite and subvolcanic trachydacite bodies (27.5–29.5 Ma).

Several trachyrhyodacite to trachyrhyolite domes representing the last stage of Bryastovo latite volcano (Gradishte and Cherniya Kamak, Yanev & Pecskay 1997) as well as rhyolite to trachyrhyolite domes from Tatarevo caldera (Yordanov et al. 2008b) – Mineralni Bani and Hisar, have been studied to characterize the extracaldera (regarding to the larger Borovitsa caldera) acid volcanics in BR. Their phenocryst association includes quartz, plagioclase, sanidine, biotite ± amphibole and diopside. The Mineralni Bani rhyolite contains no amphibole and diopside.

Three groups of volcanoes were distinguished in the MAR. They have different composition and get younger from NE to SW (Yanev et al. 1983): Maritsa, Arda and Ustren.

- Maritsa group includes the Priabonian dome-volcano Lozen (Yanev et al. 1975) composed by the products of two stages, represented by rhyolite to trachyrhyolite (with phenocrysts of quarts, plagioclase, sanidine and biotite) and trachydacite to trachyrhyodacite (quartz, plagioclase, amphibole, biotite and coarse sanidine), respectively; Sheinovets caldera rhyolites, formed during several stages (Priabonian–Rupelian, I[st] and IInd acid phases) described in Ivanova et al. (2001) and Ivanova (2005) and containing quartz, two feldspars and biotite (associating with pyroxene in one of the dykes or amphibole in rhyolite clasts found in the caldera fill deposits); Sveta Marina rhyolite dome from the IInd Rupelian acid phase containing the same phenocrysts.

- From Arda group we have studied Madzharovo trachydacite volcano and the rhyolites from the Geren dome-cluster (both formed during the IInd Rupelian acid phase) with phenocrysts of plagioclase, sanidine, biotite, diopside–augite (in Madzharovo) and

quartz (in Geren). Some acid volcanoes from the complex edifices of IInd and IIIrd Rupelian phases as Sveti Iliya and Dambalak (Dambalak, Ormanlar, Perperek, Studen Kladenets, Hisar); one body of black perlite from the west slope of Sveti Iliya volcano in the valley of Nanovitsa River (vicinity of Tsarkvitsa, Postink village) are also discussed. They have trachydacitic (Hisar volcano) to trachyrhyolitic (Studen Kladenets volcano) composition. The lack of quartz phenocrysts (only in Studen Kladenets quartz subphenocrysts are present, Yanev 2003b) is typical of the rocks from this group. Diopside–augite is very common; sometimes amphibole is also present (in Studen Kladents). Sanidine is absent from Hisar volcanics and Nanovitsa perlite. The rhyolite underlying Dambalak volcano of the IInd Rupelian acid phase as well as the numerous bodies exposed in the Nanovtsa River valley (Yordanov et al. 2008a) have not been studied.

- The Ustren group includes the Ustra dome-cluster (that includes Schupenata Planina and Ortakaya domes), some separated domes (Mishevsko, Shterna) and Zli Vrah volcano, formed during the IIIrd and the IVth Rupelian acid phases. They are built by felsitic rhyolite with perlitic peripheries containing rare phenocrysts of quartz, the two feldspars and biotite. Amphibole is identified in the Mishevsko dome. There is one dome (to the east of Vodenicharsko village) built by crystal-rich rhyolite with phenocrysts contents over 50%, interpreted as a residue of a zonal magma chamber (Hildreth 2004).

Methods

The data on phenocryst composition have been obtained in 4 laboratories: Geological Institute (JEOL 733 Superprobe equipped with WDS, analyst O. Dimitrov or EDS, analysts K. Rekalov and Tz. Iliev), in the University of Paris–11, Orsay (Cameca equipped with WDS, analyst R. Pichon), University of Paris–6 and 7 (Camebax and SX-50 equipped with WDS, analysts U. Remy and M. Fialen) and University of Louven-la-Neuve, Belgium (SX-

50 equipped with WDS, analyst J. Wautier). The control analyses of the same objects in different laboratories have showed that the data are comparable.

The modified version of the program of Papike et al. (1974) on a charge-balance basis (kindly provided by P. Nimis from University of Padova, Italy) has been used for the calculation of Fe^{3+} in pyroxenes. The crystal formulae of amphiboles have been calculated using the improved version of the IMA software (Leake et al. 1997). The temperatures have been calculated using the method of Fuhrman & Lindsley (1988) based on the distribution of the albite molecule in the feldspars. As reliable are taken only these values showing differences between individual feldspar pairs lower than 20°C (the authors recommend 4 times higher threshold i.e. 80°C).

The new calculation schema of Ridolfi et al. (2010) has been used to estimate pressure, temperature, oxygen fugacity, and water contents of the melts during amphibole crystallization. The pressure data have been compared with these obtained, using the method of Johnson & Rutherford (1989). Magnetite–ilmenite pairs (Stormer 1983) have also been used to estimate the oxygen fugacity in some samples, calculated with the program of Lepage (2003).

Chemistry of the rock-forming minerals

Clinopyroxenes

Clinopyroxene phenocrysts are relatively rare in the acid volcanics and normally occur in small amount. In BR they are identified in the 1st stage ignimbrites, in the 2nd stage black perlites, in a body emplaced in the caldera bounding faults (4th stage), in one dome of the 5th stage (Yailadere) as well as in some of the extracaldera domes (Hisar in Tatarevo caldera and Gradishte). In MAR, clinopyroxenes occur in one of the dykes of the Sheinovets caldera (Ivanova 2006) and in some of the Arda group volcanics. Clinopyroxenes from Perperek have not been analyzed since they are completely altered.

Clinopyroxenes are small, euhedral; some are slightly rounded due to magmatic corrosion. According their composition they are (Fig. 2; Appendix):

- Diopside to diopside–augite in Borovitsa caldera;
- Diopside–augite (in some volcanics in MAR) to Fe-augite (in Studen Kladenets volcano).

All clinopyroxenes analyzed are poor in Al (excluding the pyroxene in the 4th stage of
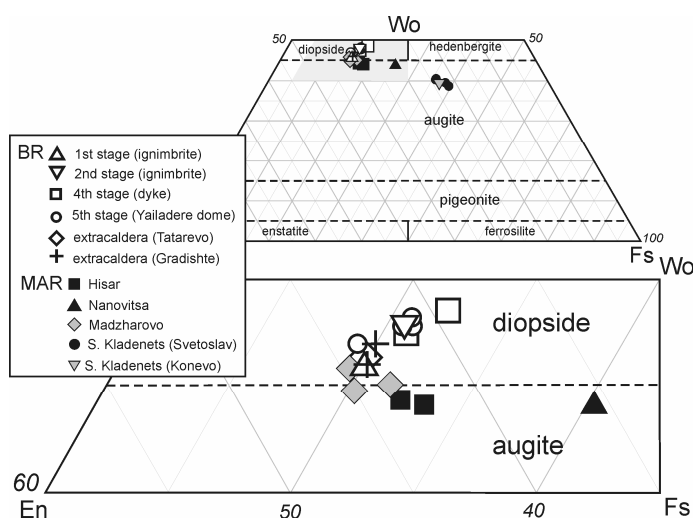

Fig. 2. Ca–Mg–Fe systematics of the clinopyroxenes from the Eastern Rhodopes acid volcanics. Below – detailed part of the diagram

BR), but rich in Ca and Si (excluding the pyroxenes from the 4th stage and from Studen Kladenets). Nevertheless they are Al-poor, Al deficiency in Si–Al tetrahedra is detected only in pyroxenes from extracaldera domes of BR, Hisar, Nanovitsa, and especially in the augite from Studen Kladenets where it reaches 0.035 *apfu*. This deficiency is balanced by Fe^{3+} as it was proved by Hartman (1969). The presence of ^{VI}Al in the rest of the pyroxenes (Fig. 3a) results in formation of tschermak molecule ($Ca^{VI}Al^{IV}AlSiO_6$). Small amount of jadeite molecule ($Na^{VI}AlSi_2O_6$) occur in the pyroxenes where $^{VI}Al > ^{IV}Al$ (1st stage ignimbrites and 2nd stage black perlites of BR and Madzharovo). Both molecules are typical for the high-pressure pyroxenes (Kushiro 1969; Thompson 1974). It was experimentally demonstrated that the $^{VI}Al/^{IV}Al$ ratio in silicate melts (and in

crystallizing from them pyroxenes, respectively) increase with growing pressure due to an increase of Al coordination in the melt (Velde & Kushiro 1978). The decrease in ^{VI}Al contents in pyroxenes from 1st to 5th stage of the Borovitsa caldera (Fig. 3a) could indicate swallowing of the acid magma reservoirs (see below: the average pressure calculated using amphibole chemistry for the 2nd stage is 0.83 kbar and for the 5th – 0.76 kbar). A negative correlation between the two types of Al has been observed in the acid volcanics of Madzharovo only.

As regarding Na, the highest contents have been registered in the pyroxenes from Madzharovo (up to 0.092 *apfu*, Fig. 3b). In BR, its contents decrease from 0.047 (1st stage), 0.038 (2nd stage) to 0.025–0.006 *apfu* (5th stage), that corresponds well with the quantity
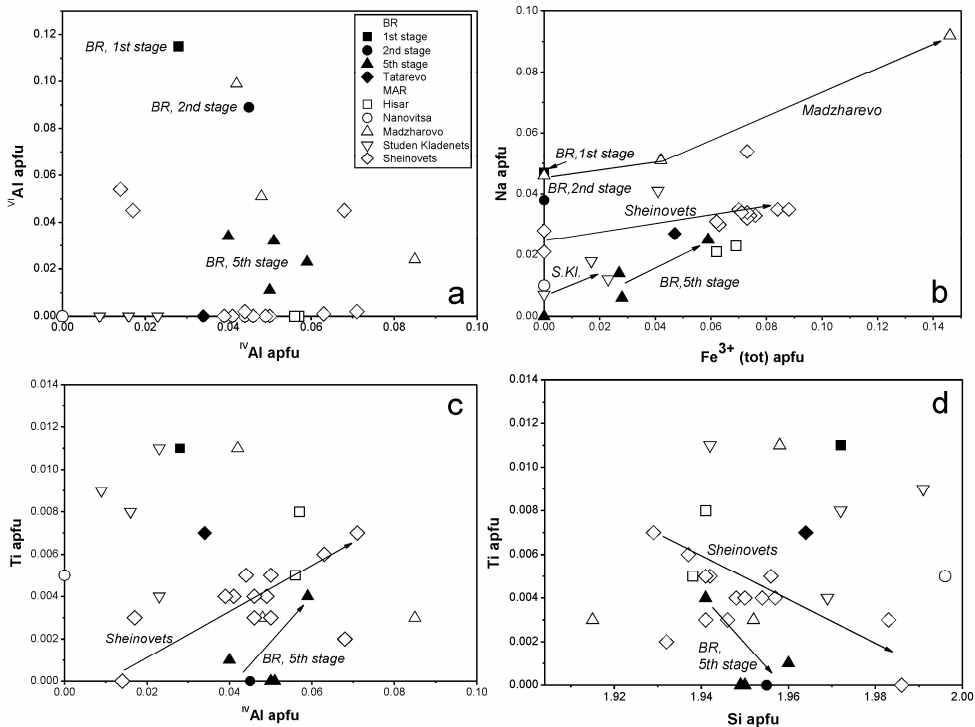

Fig. 3. Plots for the studied clinopyroxenes: a) ^{IV}Al *vs.* ^{VI}Al; b) Na *vs.* Fe^{3+} (tot); c) Ti *vs.* ^{IV}Al; d) Ti *vs.* Si. (BR) Borovitsa region; (MAR) Momchilgrad–Arda region. The arrows indicate the different trends

of ^{VI}Al and also reflects the decrease of pressure in the course of magma system evolution. Na enters the pyroxene structure as acmite component ($NaFeSi_2O_6$) explaining the positive correlation between Na and Fe^{3+} observed in the pyroxenes from almost all samples. That correlation is very clear in the pyroxenes from Madzharovo and Sheinovets. The rest of Na forms jadeite component when ^{VI}Al>^{IV}Al, as it was mentioned above. NATAL component ($NaTiSiAlO_6$, Papike et al. 1974) does not form in the pyroxenes discussed here so no correlation between Na and Ta has been observed (not shown here).

The quantity of Ti is also very low, as relatively higher values are detected in the pyroxenes from Madzharovo, Studen Kladenets and the 1st stage ignimbrites in BR (up to 0.011 *apfu*). Ti forms TAL component together with Al ($CaTiAl_2O_6$, Papike et al. 1974). That explains why Ti correlates positively with Al (Fig. 3c) and negatively with Si (Fig. 3d), better expressed only in the pyroxenes from Sheinovets and the dome of the 5th stage. It is a consequence from the most important non-quadrilateral substitution in pyroxenes ($TiAl_2 \leftrightarrow MgSi_2$).

Amphiboles

Amphiboles are more common as mafic phenocrysts in acid lavas than pyroxenes. In BR they are present in the 2nd stage ignimbrite-like volcanics, in the 4th stage caldera dykes and especially in the 5th stage domes as well as in most of the extracaldera domes (Gradishte, Cherniya Kamak, Tatarevo). In MAR they occur in the rhyolite lithics in Sheinovets caldera fill deposits, in the 2nd stage volcanics of the Lozen volcano, and in the lavas of Studen Kladenets (Konevo flow) and Mishevsko dome.

According to their chemical composition (Fig. 4a; Appendix) amphiboles are mainly Mg-hornblende and Mg-edenite (most of the edenites are not stoichiometric due to the low Si, Al and Ti contents), few are pargasite, tschermakite and Mg-hastingsite. All amphiboles have relatively higher contents of alkalis (more often between 0.4 and 0.65 *apfu* – Fig. 4b) and the richest is the edenite from the 2nd stage volcanics of BR (up to 0.9 *apfu*). K is present in all measured amphiboles, but Na is lacking in some of them (in Cherniya Kamak, and in one analysis from Gradishte). The alkalis positively correlate with Al in most of the volcanics (Fig. 4b) indicating that the occupation of A position by alkalis requires the following substitution: Na, ^{IV}Al $\leftrightarrow \square$, Si (Kostyuk & Sobolev 1969).

The high alkaline contents in amphiboles results generally from the increased alkalinity of the acid volcanism in the Eastern Rhodopes, but it can not be used to distinguish between the different magma reservoirs, since the alkali contents in the amphiboles do not reflect directly the alkalinity of magmas.

On the other hand, the alkali contents and the quantity of ^{IV}Al depend on the temperature of amphibole crystallization (Kostyuk & Sobolev 1969; Blundy & Holland 1990). This was confirmed only in amphiboles from MAR (Fig. 5). On the contrary, a negative correlation is observed between the alkali content and temperature in BR (e.g. 2nd stage volcanics).

Al and Si in edenite and Mg-hornblende vary slightly (Al between 0.82 and 1.25 *apfu*). In other types of amphiboles, as pargasite (Sheinovets caldera), Mg-hastingsite (Konevo flow of the Studen Kladenets volcano) and tschermakite (Mishevsko dome), the ^{IV}Al is very high indicating higher temperature of crystallization (Fig. 5; see also Table 3). However, some edenites from the 2nd stage of Borovitsa caldera show also high temperature despite their low ^{IV}Al content.

In contrast with the existing ideas that the quantity of ^{VI}Al in amphiboles, like in pyroxenes, increases with pressure (Leake 1965; Kostyuk & Sobolev 1969 etc.) it was proven that the total Al contents depend on the pressure (Johnson & Rutherford 1989; Blundy & Holland 1990, etc.). In the studied amphiboles ^{VI}Al normally varies between 0 and 0.32 *apfu* (Fig. 4c). The only exception is tschermakite from Mishevsko dome with
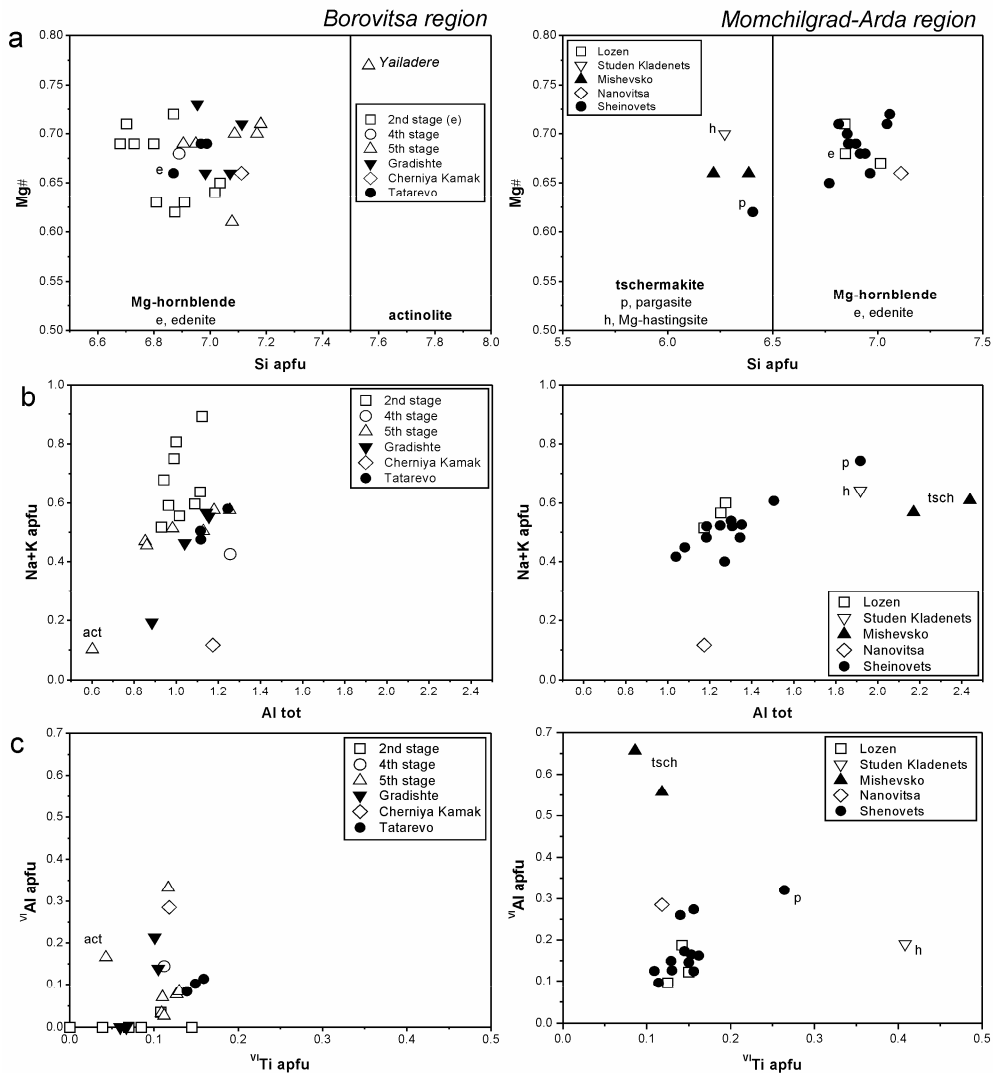
Fig. 4. Plots for the studied amphiboles: a) $Mg^{\#}$ *vs.* Si classification diagram; b) Na+K *vs.* Al_{tot}; c) ^{VI}Al *vs.* ^{VI}Ti

highest contents of ^{VI}Al (0.56–0.66 *apfu*) that was proven as xenocrystal with the program of Ridolfi et al. (2010) (see Table 4). The correlation between ^{VI}Al and $Mg^{\#}$ (Fig. 6a) observed in some places (Sheinovets, Lozen, 5th stage domes in BR, Gradishte) is part of the general substitution, existing in the amphiboles (Leake 1965):

^{IV}Al or $Na_A + (^{VI}Al, Fe, Cr, Ti) \rightarrow Ca+Mg$
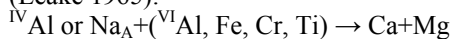
The main substitutions in Ca-amphiboles are edenite and tschermakite type (Leake 1965). The first one $[^{IV}Al + (Na+K)_A \leftrightarrow \square, Si]$ is clear and explains the negative correlation between Si and $^{IV}Al + (Na+K)_A$ (Fig. 6b) in the studied amphiboles, excepting these from the 2nd stage volcanics were it is not so well expressed. On the contrary, the tschermakite substitution $(Si+R^{2+} \leftrightarrow ^{IV}Al + ^{VI}Al)$ is manifested
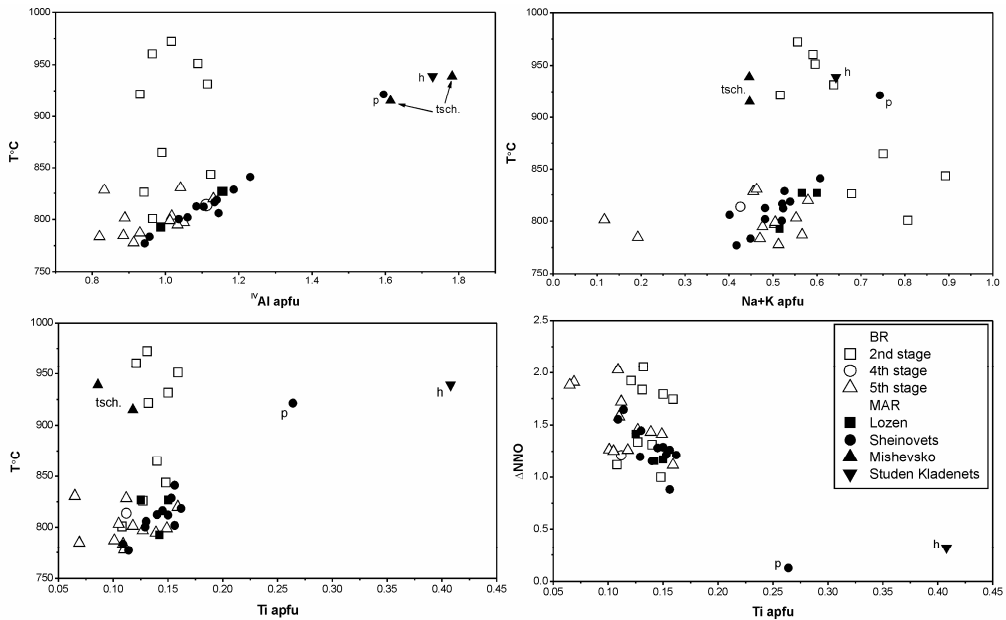
Fig. 5. Dependence of amphibole composition on temperature and oxidation potential (ΔNNO) of the melts according to the calculation schema of Ridolfi et al. (2010). (BR) Borovitsa region; (MAR) Momchilgrad–Arda region; (p) pargasite, (h) hastingsite (tschermakite xenocrysts of Mishevsko dome are not shown)

only in MAR and 5th stage domes in BR (Fig. 6c). A positive correlation between these components is registered in the Gradishte dome (BR) probably reflecting another type of substitution.

There is a clear positive correlation between tetra- and octahedral cations (Fig. 7a), very close to the linear regressive line (excluding the non-stoichiometric edenite from the 2nd stage in BR). The weak priority of the octahedral cations in most of the amphiboles could be explained with the presence of traces of Ti-richterite and/or Ti-ribekite types of substitution (Kamenov et al. 2002).

TiO$_2$ is relatively low (Figs. 4c, 7b): 1–1.5 wt.% in BR and a bit greater – in MAR. The highest values are registered in Mg-hastingsite from Studen Kladenets (3.8%). Ti balances the tetrahedral deficiency, if it is present (as in the non-soichiometric edenite of the 2nd stage of BR and Gradishte). A clear positive correlation between Ti and ^{IV}Al (Fig. 7b) is observed in

some of the amphiboles (Sheinovets, extra-caldera domes of BR) resulting from the presence of the following variety of the tschermakite substitution: Ti+2^{IV}Al→Mg+2Si. The Ti contents correlate positively with the temperature of crystallization (in MAR only) and negatively – with the oxygen fugacity (Fig. 5), as it was experimentally demonstrated (Ernst & Liu 1998, etc.).

A feature common for both regions is the low values of Fe$^#$ (Fe^{3+}/Fe^{2+}+Fe^{3+}), varying between 0 and 0.35 (Fig. 7c). These values correlate generally with the oxygen fugacity (expressed by the positive diversion from the NNO buffer) as the last is relatively higher in the BR magmas (Fig. 5). In some of the rocks (e.g. the 2nd stage volcanics of Borovitsa, Tatarevo, Gradishte and in all MAR volcanics, excluding xenocrystals from the Mishevsko dome) Fe$^#$ correlates positively with Mg$^#$ (Fig. 7c).

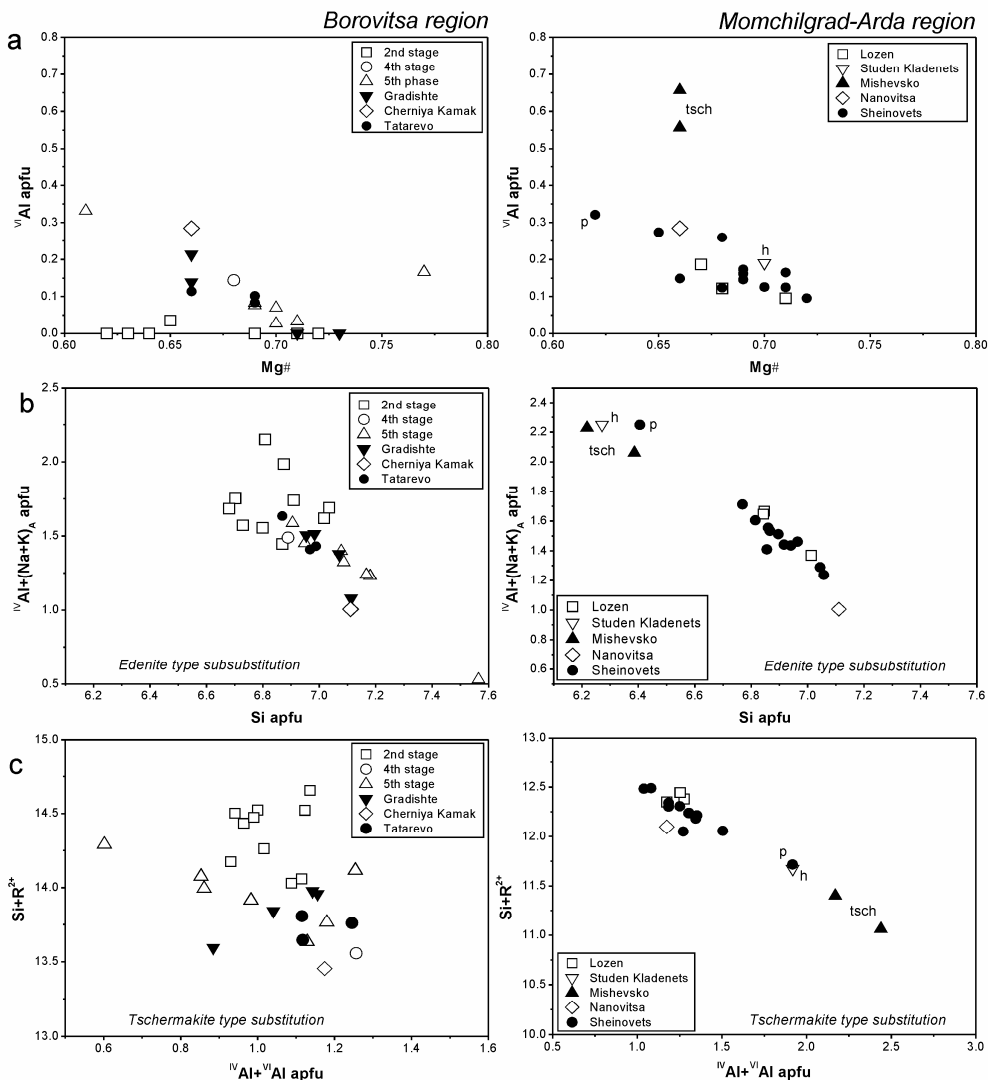Mn is more abundant in the BR lavas as its maximum quantity has been measured in

48

Fig. 6. Plots for the studied amphiboles: a) ^{VI}Al *vs.* Mg$^{#}$; b) ^{IV}Al+(Na+K)$_A$, *vs.* Si; c) Si+R^{2+} *vs.* Al$_{tot.}$ (p) pargasite, (h) hastingsite, (tsch) tschermakite

one of the 5th stage domes (1.65 wt.%) as such high Mn content is quite unusual for hornblende. On the contrary, the lowest values of Mn have been registered in the extracaldera domes (0.35%).

Biotite

Biotite is the most common and everywhere-present mafic phenocrysts in the acid volcanic rocks in the Eastern Rhodopes. According to its
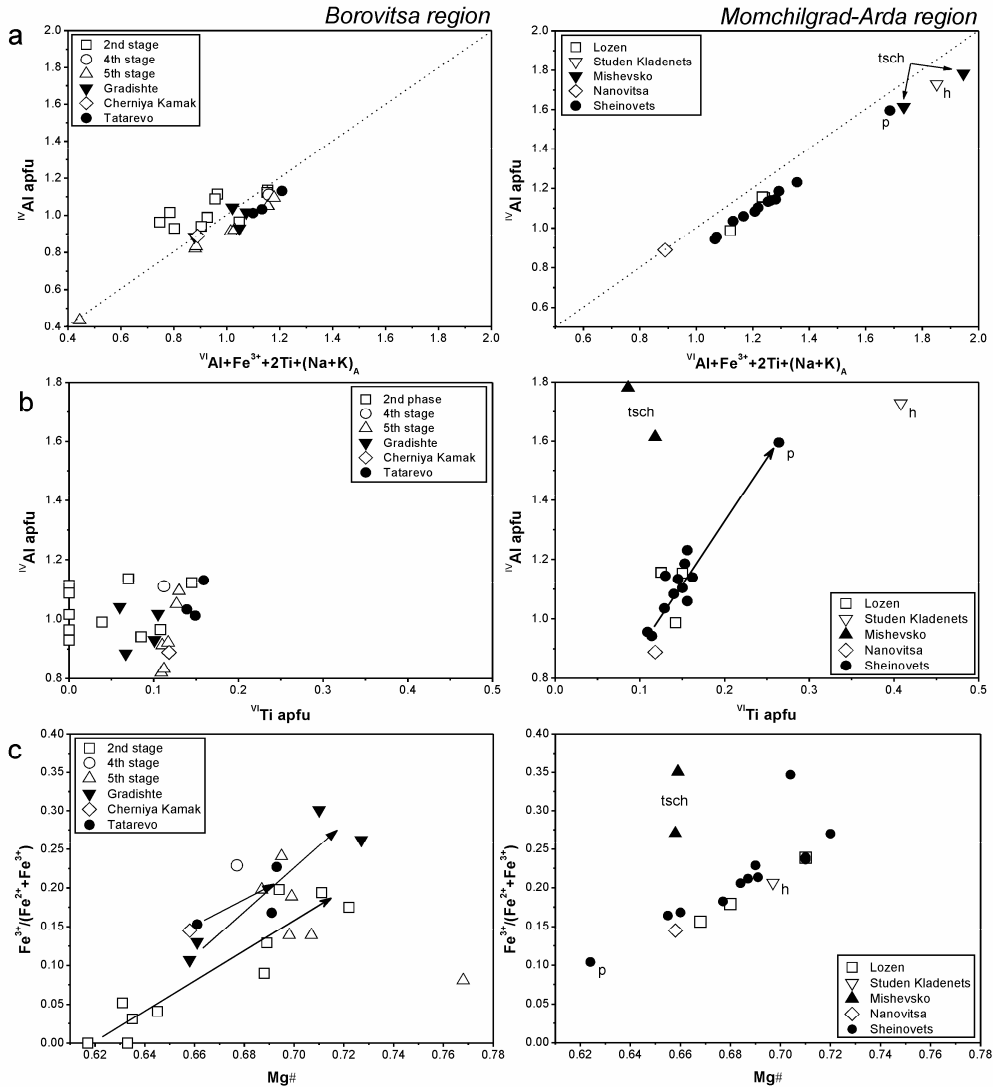
Fig. 7. Plots for the studied amphiboles: a) ^{IV}Al vs. ^{VI}Al+Fe^{3+}+2Ti+(Na+K)$_A$; b) ^{IV}Al vs. ^{VI}Ti; c) Fe$^{\#}$ vs. Mg$^{\#}$. (p) pargasite, (h) hastingsite, (tsch) tschermakite. The arrows indicate the different trends

composition (Fig. 8; Appendix), the biotite is annite (with only one exception – phlogopite, present in the 2nd stage volcanics in BR). Mg$^{\#}$ in the annites varies in a narrow range between 0.53 and 0.67 in BR. In MAR, richer in Fe (Mg$^{\#}$ 0.3–0.53) are the biotites from the Arda

group volcanoes (Studen Kladenets, Perperek and Dambalak). It is considered that the Fe contents increase very fast with the chemical potential of H$_2$O i.e. with the decrease of temperature of crystallization (Marakushev 1965; Ivanov 1970). We have not detected this
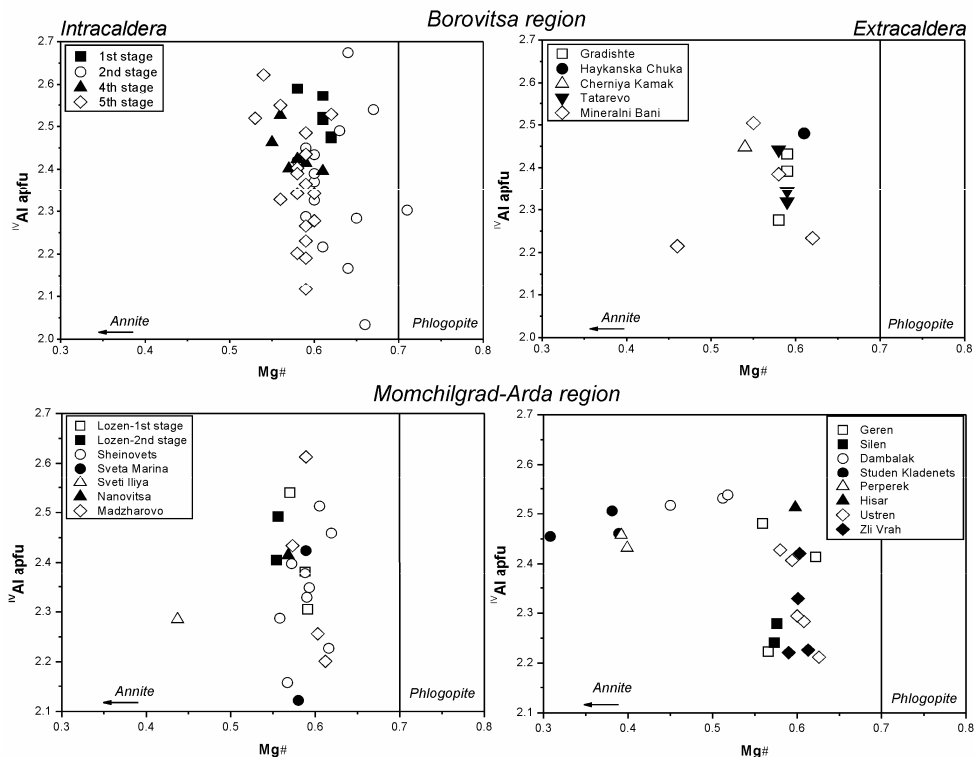
Fig. 8. ^{IV}Al *vs.* Mg$^{\#}$ classification diagram of the studied micas

trend in BR. Moreover, it is the opposite in MAR, where the highest temperature lavas from the Arda group (e.g. Studen Kladenets and Perperek) contain richer in Fe biotite phenocrysts (Fig. 8; see also Table 2).

The contents of the tetrahedral Al vary widely in BR from 1.67 to 2.67 *apfu,* and much narrower in MAR: from 2.1 to 2.55 (Fig. 9). A negative correlation between ^{IV}Al and Mg$^{\#}$ is observed in some of the studied volcanics of BR (1st and 4th stage of BR) (Fig. 8). This correlation results from the most important substitution in biotite: $(Mg,Fe)O+SiO_2 \leftrightarrow Al_2O_3$ (Marakushev 1968). Tetrahedral deficiency (Fig. 9) occurs in some of the volcanics from the Borovitsa caldera. In MAR, it appears essentially in the biotites from the Silen volcano and these from the Arda group (Fig. 9). It was experimentally demonstrated (Cruciani et al. 1995) that the tetrahedral deficiency

is compensated by Fe^{3+}. In the Eastern Rhodopes the maximum has been registered in the biotites from the 2nd stage BR volcanics, where it reaches 0.38 *apfu* calculated as Fe^{2+} (Fig. 9).

The octahedral Al (Fig. 9) is commonly present in low amounts (up to 0.2–0.3 *apfu*). It reaches higher values (up to 0.6 *apfu*) in single biotites coming from the 2nd and 5th stage volcanics of BR, Madzharovo and Nanovitsa in MAR. The biotites from Silen, Hisar, Perperek and Studen Kladenets contain no ^{VI}Al. A clear negative correlation between octa- and tetrahedral Al is observed in biotites from the Borovitsa intracaldera volcanics, which can be explained with the above-mentioned substitution. In MAR, such a correlation exists only in biotite from the Lozen volcano.

Ti contents are quasi-constant in the two volcanic regions (Fig. 10) – between 0.4 and 0.6–0.7 *apfu*. Only one analysis of biotite from
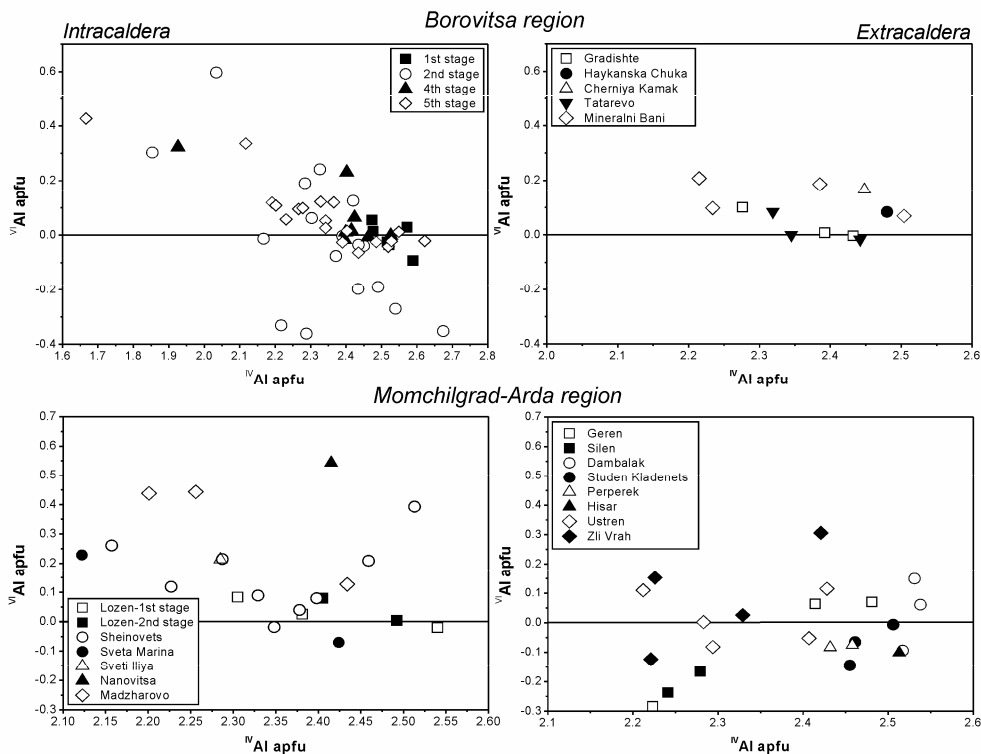
Fig. 9. Plot of ^{VI}Al *vs.* ^{IV}Al for the studied micas

the 1st stage ignimbrites of BR shows Ti content as high as 0.81% *apfu* and the lowest is measured in one biotite of the 2nd stage volcanics (0.12 *apfu*). A negative correlation between Ti and Mg$^{\#}$ is observed in the 5th stage volcanics, in Arda and Ustren group volcanics of MAR. This correlation is due to the substitution Ti+2Al↔Mg,Fe+2Si (Guo & Green 1990) that is the extended version of the main biotite substitution, given above. However, it is positive in the biotites from Sheinovets caldera.

The contents of BaO are low, commonly less than 0.1 wt.%. Only in biotites with high Ti contents (BR ignimbrites of the 1st stage, Haykanska Chuka, 1st stage of Lozen and Hisar) BaO is over 1%. An increase of Ba contents from the oldest, 1st stage, towards the younger, 5th stage, of the evolution of Borovitsa caldera has been observed (see the Appendix). A correlation between Ti and Ba

exists (not shown here) following a very complex substitution schema, involving almost all cations, proposed by Mansker et al. (1979) and Velde (1979):

$$^{XII}Ba+2^{VI}Ti+3^{IV}Al =$$
$$^{XII}(K+Na+Ca)+3^{VI}(Mg+Fe+Mn)+3^{IV}Si.$$
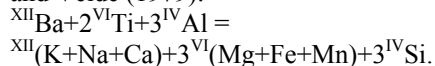
The analysis of all studied biotites confirms this substitution schema (Fig. 11).

Only F from the volatiles in the biotite phenocryst has been studied (see the Appendix). No regularities in the average F contents distribution have been observed in BR where it varies from 0.25 to 0.49 wt.%. An increase of F contents from the oldest Priabonian towards the youngest, Rupelian phase has been observed in MAR: the average F content in biotite in the individual Priabonian volcanoes is 0.14 and 0.29%, in the volcanoes the IInd Rupelian phase – 0.28 and 0.68%, in the IIIrd phase – 0.48%, in the IVth – 0.94%
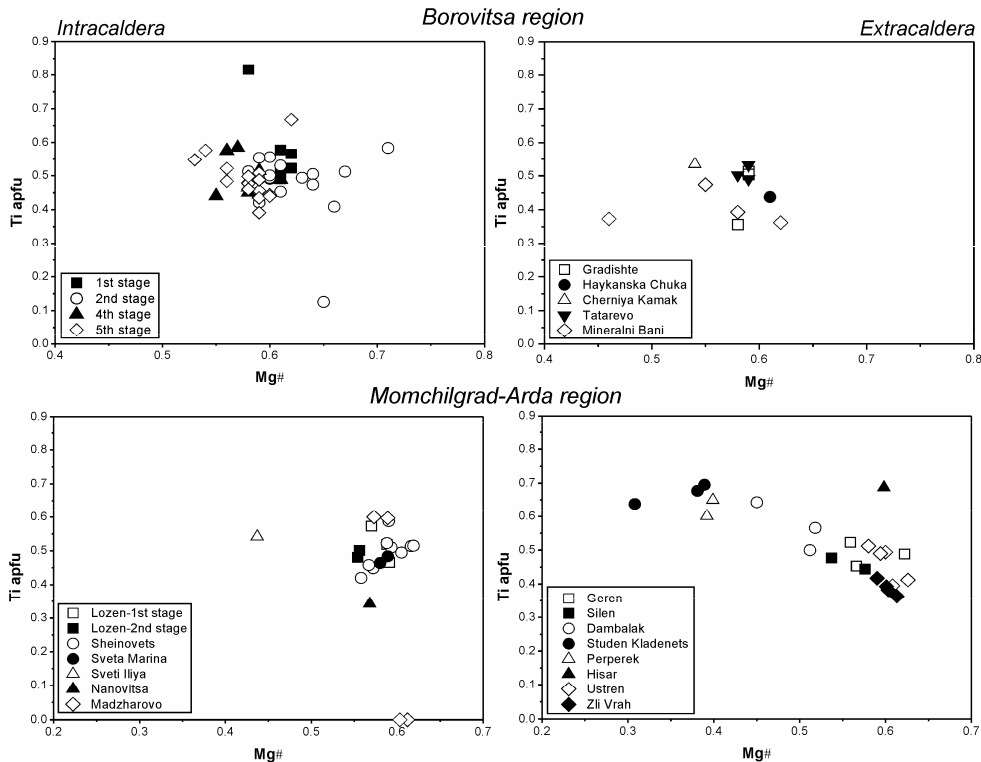
Fig. 10. Plot of Ti *vs.* Mg$^{\#}$ for the studied micas
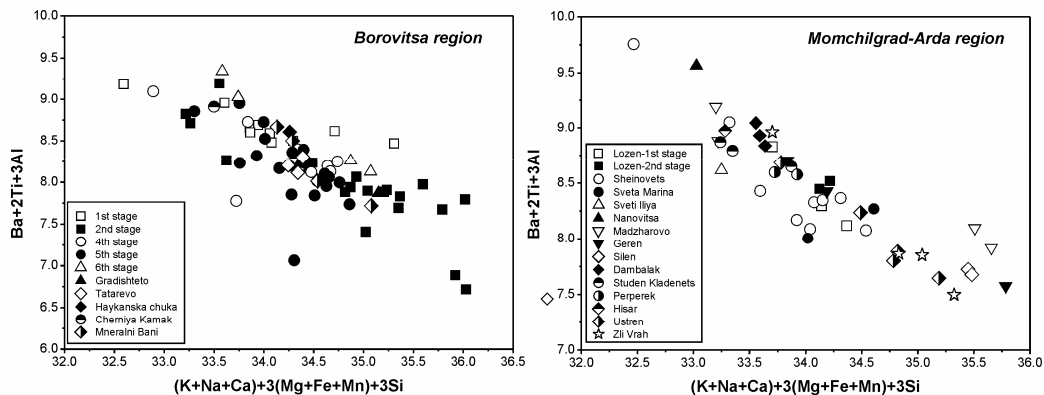
Fig. 11. Substitution mechanism of Mansker et al. (1979) and Velde (1979) in biotites with the points of the studied micas from the two volcanic regions

with the highest observed F content of 1.34% (in Zli Vrah volcano). This distribution pattern confirms an earlier assumption (Yanev et al. 1983) that F had an increasing influence in water-bearing fluids during the generation of acid magmas in MAR – from the oldest to-

wards to youngest volcanics or from NE to SE, respectively (Fig. 1). Such an increase of the F contents results in shifting of the eutectic minimum of the crystallizing magma towards higher albite contents (Manning 1981). In MAR, this is expressed by an increase of Na_2O/K_2O+Na_2O ratio from the oldest towards the youngest volcanic rocks (Yanev et al. 1983).

Feldspars

The feldspars are represented by plagioclase (acid oligoclase to labradorite and even bytownite in the Sheinovets caldera, Ivanova 2006) and sanidine (rarely up to Na-sanidine) (Fig. 12; Appendix). Sanidine is absent from the phenocryst assemblage of the most basic volcanics (trachydacite from the Hisar volcano) as well as from perlite of Nanovitsa. Anorthoclase (in the younger volcanics from Zli Vrah and Silen) to Ca-anorthoclase (some domes of the 5th stage of BR and in Sheinovets lavas, Ivanova 2006) is also present as subphenocrysts, microlites, or as coating of sanidine.
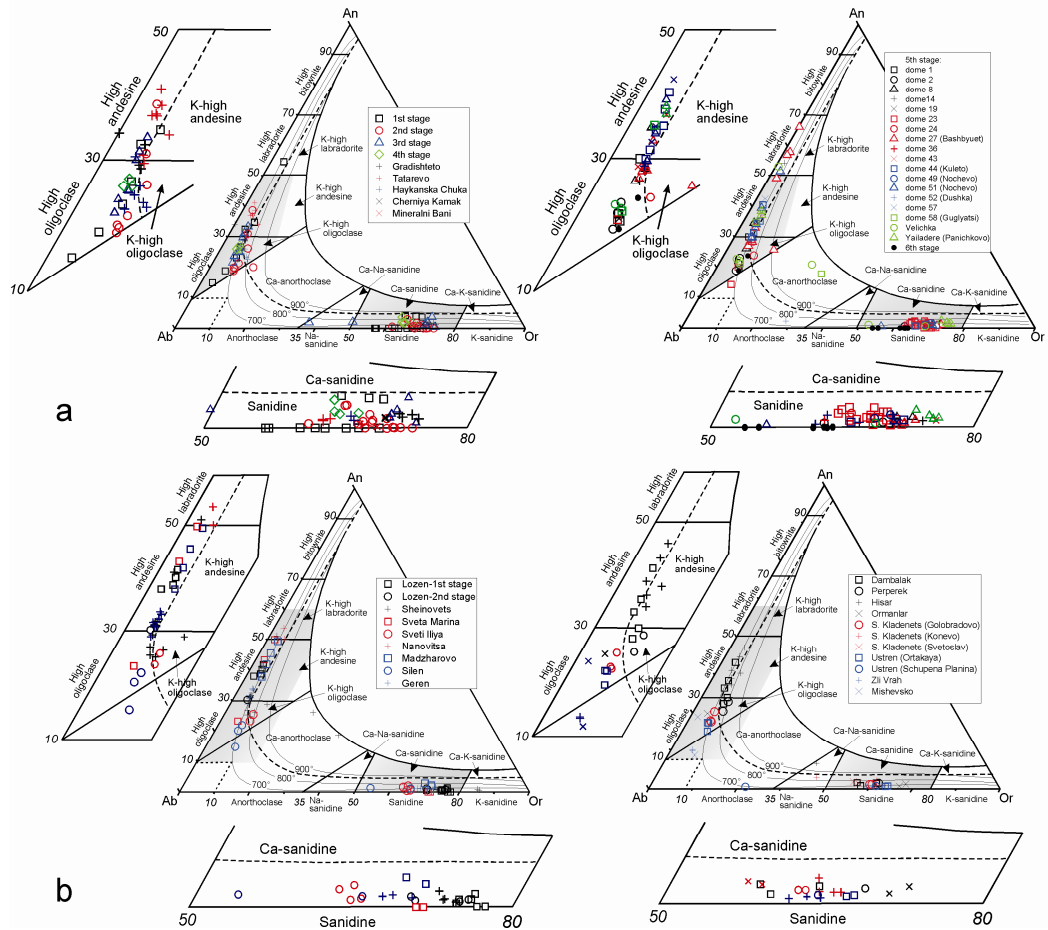

Fig. 12. Systematics of the disordered feldspars (according to Smith & Brown 1988) from the Eastern Rhodopes acid rocks: a) in Borovitsa region; b) in Momchilgrad–Arda region. Temperature curves are after Fuhrman & Lindsley (1988). The gray-shaded fields are enlarged for a better view

The feldspars are commonly euhedral, as only sanidine can sometimes be slightly corroded (rounded) by the melt – a phenomenon typical of acid volcanics. It is explained with changes of partial pressure of water in melt, resulting in shifting of the liquidus line and eutectic minimum, leading to unequilibrium between already crystallized feldspars and the melt (Marakushev & Yakovleva 1975). The plagioclases are weakly zoned, excluding these from one of the Sheinovets caldera bodies (Ivanova 2006) where phenocrysts composed by both plagioclase (with varying Na contents) and adularia were identified. Some sanidines have zonal structure due to variations in Ba contents. Numerous zones (Fig. 13a) with irregularly varying Ba quantities are observed in strongly corroded and fragmented sanidine in one of the 1st stage ignimbrite sheets from the central parts of the Borovitsa caldera. As high as 8.9 wt.% BaO ($Cn_{17.1}$) was measured in the central parts of some crystals. In other ones the richest in Ba are their rims (Fig. 13b). Ba varies within the zones too. This could be due to different ratios between kinetic and diffusion regime of melt crystallization (Vesselinov 1998).

A negative correlation between Si/Al ratio and Ba has been detected in the Ba-rich sanidines from 1st stage ignimbrites and some of the 5th stage domes in BR, as well as in Lozen, Gerena, and Sheinovets in MAR (Fig. 14). This correlation indicates the heterovalent substitution $Ba^{2+}Al^{3+} \leftrightarrow K^{+}Si^{4+}$ (Afonina et al.
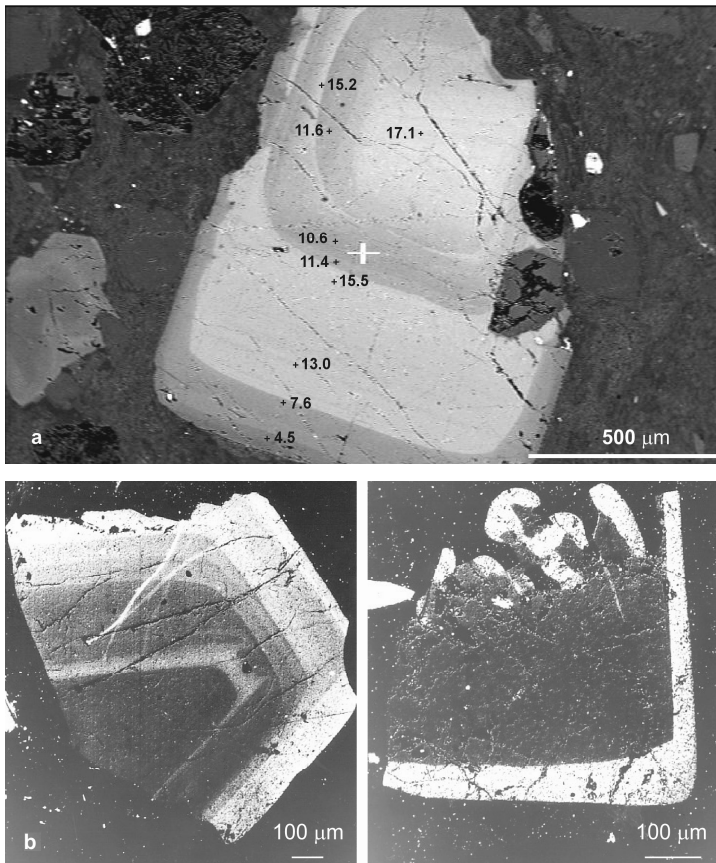
Fig. 13. Back scattered images of zonal Ba-sanidine phenocrysts in one of the 1st stage ignimbrite sheets in Bororvitsa caldera: a) with celsian molecules in the different zones of one phenocryst (Cameca SX-50, WDS analyses in the University of Louven-la-Neuve, Belgium); b) with no quantitative data on Ba contents (JEOL 733 superprobe, Geological Institute of BAS, Sofia)
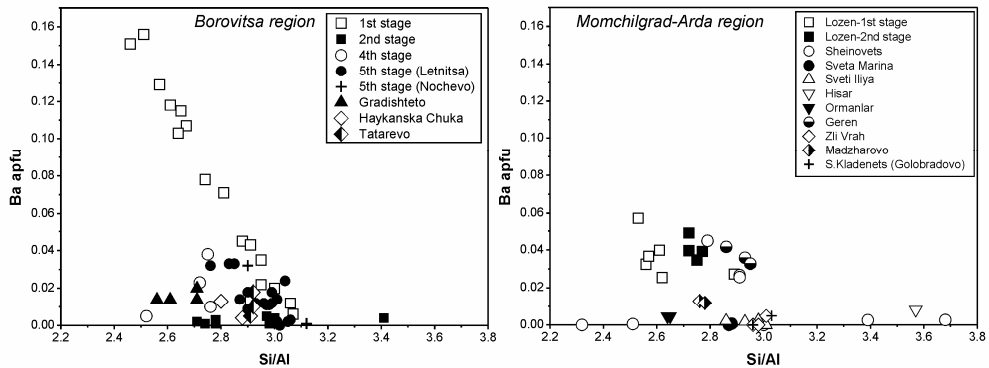
Fig. 14. Plot of Ba *vs.* Si/Al for the Eastern Rhodopes sanidines

1978). At lower Ba contents it is not visible, probably due to the analytical inaccuracy resulting from detection limits of the microprobe. A clear positive correlation between Ba and Sr has also been detected (Fig. 15).

From the comparison of the contents of Ba in sanidine and biotite (Fig. 16) it is evident that Ba preferably enters the sanidine in the 1st stage ignimbrites of BR. However, Ba prefers biotite in the 2nd stage volcanics and distributes equally between these two minerals in the 5th stage domes.

The study of plagioclase phenocrysts showed that basic plagioclase (reaching up to acid labradorite, Table 1) and even to bytownite (Ivanova 2006) are present in some areas (Shenoviets, Sveta Marina and some of the 5th stage domes in BR) together with the acid plagioclases typical of acid lavas. The basic plagioclases appear as strongly corroded cores in more acid crystals (in Shenovets), but also as sieve-textured phenocrysts in the other two areas. This is an evidence of mixing between acid rhyolite melt and more basic, probably latite one.

Quartz

Quartz participates in the phenocryst associations in most of the Eastern Rhodopean acid volcanoes. The volcanics of Arda group as well as the 1st stage ignimbrites of BR do not contain quartz phenocrysts, since they are rela-

tively more basic. However, even in some of them (as Studen Kladenets and BR ignimbrites) rare quartz subphenocrysts are present.

Normally quartz crystals are corroded by the melt probably as a result of magma emplacement at shallow levels, where the melt degases (releasing parts of water and CO_2 dissolved in the magma), resulting in its alkalization, leading to loss of equilibrium with already crystallized quartz (Marakushev & Yakovleva 1975).

Table 1. *Two populations of plagioclase phenocrysts in some Eastern Rhodopes acid volcanics*

Borovitsa region (intracaldera volcanics)		
Stage	An of plagioclase	
1st stage	An 55.0	An 35.0
5th stage: dome 14	An 54.6	An 28.4
dome 27	An 66.3	An 26.0
dome 51	An 51.8	An 30.0
dome 70	An 53.3	An 22.8

Momchilgrad–Arda region		
Volcano or caldera	An of plagioclase	
Sheinovets caldera*	An 78.4	An 25.9
Sveta Marina	An 50.3	An 23.4
Madzharovo volcano	An 49.7	An 37.9
Nanovitsa perlite	An 54.1	An 29.1

* according to Ivanova (2006)
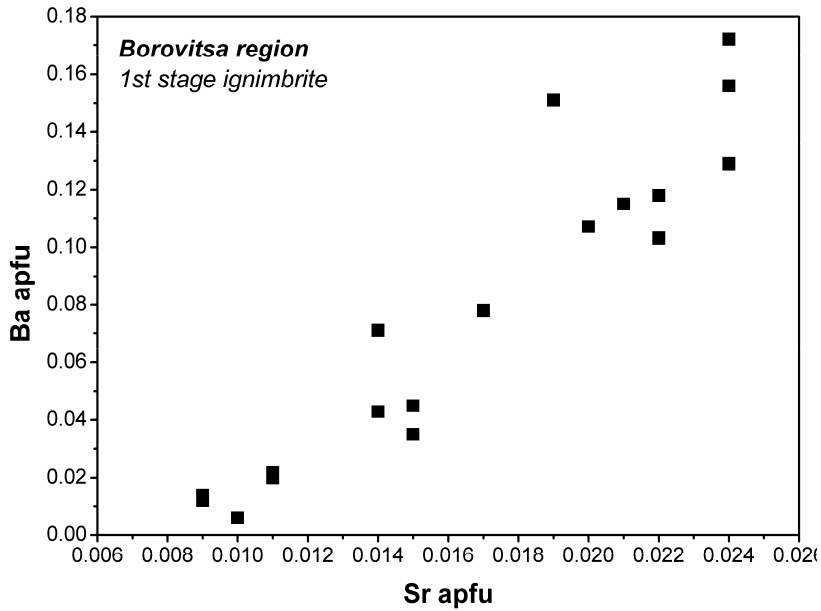
Fig. 15. Plot of the Ba *vs.* Sr contents from the sanidine phenocryst on Fig. 13a, 1st stage ignimbrite sheet, Borovitsa caldera (WDS analyses in the University of Louven-la-Neuve, Belgium)
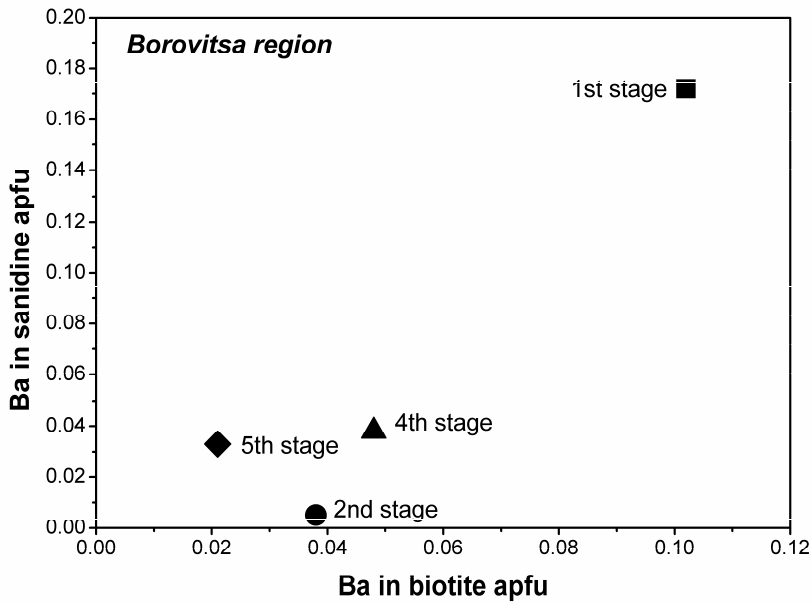
Fig. 16. Distribution of Ba between biotite and sanidine in some acid volcanics of the Borovitsa caldera

Oxide minerals

Together with apatite, zircon and titanite, the oxide minerals are the main accessory minerals in the Eastern Rhodopean acid volcanic rocks.

The oxide phases in non oxidized glassy volcanics (black, grey and white perlites) have only been measured (see the Appendix). They are oxides of Ti–Fe^{2+} and Ti–Fe^{2+}–Fe^{3+}. The last form one almost continuous row from Ti-

magnetite to magnetite–hematite (up to the ratio $Fe^{2+}:Fe^{3+}=30:70$), quite different from that observed in the basic volcanics (Fig. 17). Probably that corresponds to the higher oxygen fugacity in the acidic melts, as it is indicated by the calculations below.

Ti-magnetite (with TiO_2 of 21 wt.% in Letnitsa dome of the 5th stage) to almost pure magnetite–hematite (with TiO_2 of 0.5% in Mineralni Bani dome) have been found in the samples from BR. The magnetite–hematite indicates high oxygen fugacity (1.12–2.03 above the NNO buffer according to amphibole oximeter of Ridolfi et al. 2010, see Table 3). Mn, Mg and Al contents are low, reaching up to 1.8, 1.0 and 1.7%, respectively. Ilmenite is identified only in the black perlite of the 2nd stage of the Borovitsa caldera, having higher contents of Mn and Mg (2.7 and 1.4%, respectively).

Ti-magnetite (with TiO_2 of 10.3 to 18.7%

in Perperek and Svetoslav, respectively) to Ti-poor magnetite–hematite (with TiO_2 of 4–6% in Ustren area, Konevo and Dambalak) has been identified in MAR. Unlike BR, in MAR they are richer in Mn and Al (i.e. of jacobsite and hercinite molecule): MnO up to 6.4% (Silen) and Al_2O_3 up to 2.65% (Perperek), but poor in Mg (0.01–0.57%). Ilmenite has also been found (in Ustren area) as well as a mineral, close to ferropseudobrookite (Studen Kladenets and Perperek). In Studen Kladenets, according to the data from amphibole oximetry of Ridolfi et al. (2010) this phase is crystallized at one of the lowest values of the oxygen fugacity measured in the studied rocks (0.32 above the NNO buffer, see Table 3). These Ti-phases are rich in Mn, Al and Mg: 6.05% (Ustren area), 2.65% (Perperek) and 1.4% (Ustren area), respectively. No correlation between Mn and the major oxides in the above mentioned phases exists.
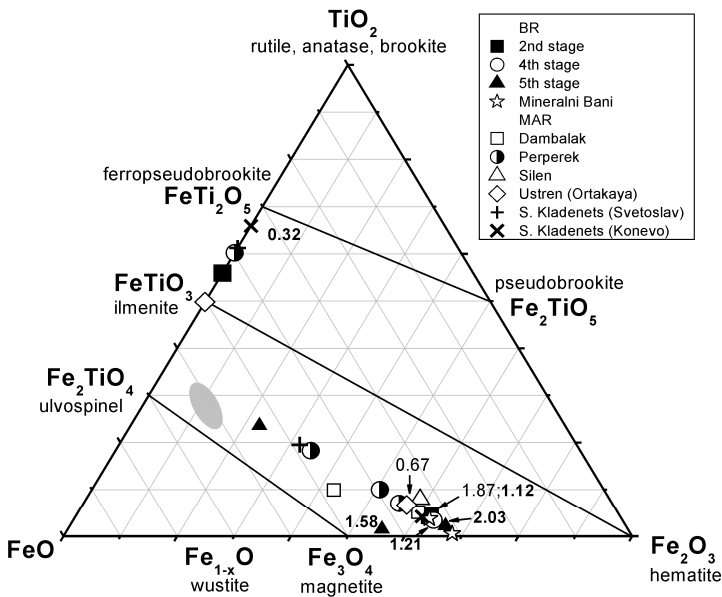
Fig. 17. Fe–Ti oxide systematics (Baddington & Lindslay 1964) with the points of the studied oxide minerals from the Eastern Rhodopes acid volcanics (the numbers indicate ΔNNO: the values obtained using the amphibole oximeter of Ridolfi et al. (2010) are given in bold, these, obtained by the magnetite–ilmenite oximeter are in regular font). The gray-shaded field is the Ti-magnetites from Cameroon basic rocks (Wandji et al. 2010), plotted for comparison

Table 2. *Two-feldspar temperatures of Eastern Rhodopes Paleogene acid volcanics (^{o}C at 1 kbar)*

MAR		Borovitsa region			
Volcano	$T°$C	stages	$T°$C	extracaldera	$T°$C
Lozen (1st)	709	2nd	722–726	Gradishte	692–699
Lozen (2nd)	740	3rd	721–729	Mineralni Bani	714–750
Sheinovets	711–725	4th	721	Tatarevo	783
Sveta Marina	730	5th (different	688–690.5		
Madhzarovo	778–809	domes)	696–697		
Geren	772		712.5–714		
S. Kladenets (Golobradovo)	776		695		
			695		
Sveti Iliya	815		616–715		
Perperek	805		695–735		
Dambalak	845		691–692		
Ustren area			720		
(Ortakaya)	730		727–729		
(Shterna)	648		717		
Zli Vrah	670		722		

Estimation of temperature, pressure, oxygen fugacity and water contents in the acid melts

In order to estimate the temperature of crystallization of phenocryst minerals the amphibole geothermometer of Ridolfi et al. (2010) and feldspar geothermometer of Fuhrman & Lindslay (1988) have been used. The obtained results are listed in Tables 2 and 3. These data, especially concerning amphibole, confirm the speculation made on the basis of phenocrysts chemistry (see above), proposing a decrease of temperature together with the evolution of the Borovitsa caldera volcanism, unlike the evolution in most of the calderas in the world. The amphiboles from the 2nd stage crystallize at temperatures of about 800–970°C, from the 4th – 814°C, from the 5th – 778–828°C. The feldspars from the 2nd, 3rd and 4th stage crystallized at about 721–729°C, from the 5th – 616–735°C. This could be due to magma drainage from increasingly higher levels of the magma chamber, resulting in a homodrome trend of evolution of the caldera volcanics (Yanev 1990, 1998).

In MAR, the highest temperatures of crystallization have been obtained for the feldspars from the Arda group of volcanoes (770–850°C), the lowest – for the feldspars from the Ustren group (650–730°C). The highest temperatures of amphibole crystallization also come from the Arda group (Studen Kladenets – 940°C) as well as from the xenocrysts of Mishevsko dome. It was confirmed that the pyroxene-containing lavas have the highest temperatures, and amphibole-containing ones – lower temperature. In an older study (Yanev 1998) a "temperature border" was traced on the basis of the presence and lack of these two minerals. According to the SiO_2 content (78 and 72 wt.%) these border values are 700°C and 720°C (temperatures of feldspar crystallization), respectively.

It was also supposed that the pressure is in linear dependence of the Al contents in amphiboles (e.g. Johnson & Rutherford 1989, etc.). However, it became evident that this dependency is exponential (Ridolfi et al. 2010) and using this improved equation the following values for the pressure have been obtained (Table 4):

Table 3. *Calculated temperatures, oxygen fugacity and water contents of magma during amphibole crystallization, according to the method of Ridolfi et al. (2010)*

Region	Momchilgrad–Arda				Borovitsa									
					intracaldera					extracaldera				
Volcano or caldera	T°C	lgfO_2	ΔNNO	H_2O wt.%	stages	T°C	lgfO_2	ΔNNO	H_2O wt.%	locality	T°C	lgfO_2	ΔNNO	H_2O wt.%
Lozen volcano (2nd stage)	827	-12.13	1.17	4.18	2nd – ignimbrite-like rocks and perlites	801	-12.73	1.12	2.70	Gradishte dome	785	-12.30	1.91	3.71
	827	-11.88	1.42	4.12		922	-9.50	2.06	3.65		830	-11.36	1.88	3.61
	793	-12.85	1.16	4.79		972	-8.89	1.84	3.92		787	-12.87	1.27	4.07
Sheinovets caldera*	783	-12.67	1.55	4.67		960	-8.99	1.92	3.37		803	-12.54	1.25	4.17
	829	-12.04	1.22	4.90		932	-9.59	1.79	3.57	Ch. Kamak dome	801	-12.57	1.26	6.18
	812	-12.31	1.29	4.52		951	-9.31	1.74	3.74					
	777	-12.72	1.65	4.59		865	-11.26	1.31	2.87	Tatarevo caldera	795	-12.54	1.44	4.15
	818	-12.25	1.21	4.68		844	-11.97	1.00	2.61		799	-12.47	1.41	3.85
	816	-12.23	1.28	4.83		826	-11.99	1.34	3.24	(Hisar dome)	820	-12.32	1.12	3.99
	812	-12.43	1.15	5.47	4th – dyke	814	-12.36	1.21	5.04					
	841	-12.11	0.88	5.19	5th – domes	797	-12.47	1.45	4.01					
	806	-12.28	1.45	5.00		778	-12.77	1.58	3.75					
	800	-12.66	1.20	4.52		784	-12.20	2.03	3.93					
	921	-11.35	0.13	6.21		828	-11.57	1.72	3.69					
	802	-12.66	1.26	4.73										
S. Kladenets volcano	939	-10.86	0.32	6.82										
Mishevsko dome**	915	invalid***												
	939	invalid												

*including the amphiboles of Ivanova (2006)

**xenocryst

***when defined as xenocryst (Altot>0.21) only T°C is calculated

Table 4. *Calculated pressures (in kbar) and corresponding depths of the amphibole crystallization*

Region	Momchilgrad–Arda			Borovitsa							
					intracaldera				extracaldera		
Volcano or caldera	J&R (1989)	Ridolfi et al. (2010)	depth km (cont. crust)	stages	J&R (1989)	Ridolfi et al. (2010)	depth km (cont. crust)	locality	J&R (1989)	Ridolfi et al. (2010)	depth km (cont. crust)
Lozen volcano (2nd stage)	1.94	1.19	4.5	2nd – ignimbrite-like rocks and perlites	0.77	0.81	3.0	Gradishte	0.29	0.69	2.6
	1.84	1.15	4.4		0.84	0.72	2.7	dome	0.94	0.86	3.2
	1.51	1.03	3.9		0.62	invalid	invalid		1.37	0.99	3.7
Sheinovets	1.11	0.90	3.4		1.25	0.81	3.1		1.43	1.01	3.8
caldera*	2.26	1.32	5.0		0.47	0.75	2.8	Ch. Kamak dome	1.51	1.02	3.9
	1.83	1.14	4.3		1.35	0.94	3.6				
	0.93	0.84	3.2		1.14	0.91	3.4	Tatarevo	1.26	0.95	3.6
	2.05	1.23	4.7		0.73	0.79	3.0	caldera	1.25	0.95	3.6
	2.07	1.24	4.7		1.29	0.96	3.6	(Hisar dome)	1.81	1.14	4.3
	2.22	1.31	4.9		0.52	0.74	2.8				
	2.90	1.65	6.2	4th – dyke	1.85	1.16	4.4				
	1.92	1.17	4.4	5th –	1.31	0.96	3.6				
	1.55	1.04	3.9	domes	1.53	invalid	invalid				
	4.65	2.99	11.3		0.70	0.78	3.0				
	1.55	1.04	3.9		1.84	0.64	2.4				
S. Kladenets volcano	4.70	2.97	11.2		0.15	0.67	2.5				
Mishevsko dome**	5.70	invalid***									
	6.90	invalid									

*including the amphiboles of Ivanova (2006);

**xenocrysts;

***when defined as xenocryst (Altot>0.21) only $T^{\circ}C$ is calculated

(J&R) Johnson & Rutherford (1989)

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- In BR: 0.72–0.96 kbar for the amphiboles from the 2nd stage volcanics, 1.16 kbar for the 4th stage caldera dykes and 0.64–0.96 kbar for the 5th stage domes. The same pressure values were obtained for the extra-caldera domes. All amphiboles crystallized in the crustal conditions, close to the surface from 2.4 to 4.4 km.

- Regarding MAR, low to medium values for the pressures have been obtained from the amphiboles of Sheinovets (0.84–1.65 kbar, corresponding to depths of 3.2–6.2 km with one exception of 3 kbar); medium values have been obtained for the amphiboles of Lozen volcano (1.03–1.19 kbar, corresponding to depths of 3.9–4.5 km); the higher values have come from the amphiboles of Studen Kladenets (2.97 kbar and depths 11.2 km). The equation of Johnson & Rutherford (1989) has been used to calculate the pressure at which amphiboles from Mishevsko dome were formed. The obtained values are very high (5.7–6.9 kbar) supporting the assumption that they are xenocrystals. Their composition really differs from all other studied amphiboles – they are the only tschermakites in the area, and have the highest contents of both Al and $Fe^{\#}$.

Our attempts to apply the pyroxene geothermobarometer proposed by Putirka et al. (2003) failed since the pyroxenes studied contain jadeite component. The only result obtained (T=932°C and P=13.2 kbar) is for the pyroxenes from Madzharovo perlite and seems not realistic, especially regarding the pressure.

The oxygen fugacity was estimated using magnetite–ilmenite pair (Stormer 1983) found only in two bodies of black perlite: $lgfO_2$ = -12.4 at 790°C for the 2nd stage volcanics in BR and -13.8 at 789°C, respectively, for Ortakaya dome from the Ustren group. Ti-rich phase is close to ferropseudobrookite in all the others. The oxymeter of Ridolfi et al. (2010) allows including of much more samples since it calculates the oxygen fugacity in amphibole (Table 3). In BR, it is relatively equal in the 2nd stage volcanics (from 1.0 to 2.06 units above NNO buffer) and in the 5th stage domes (from

1.45 to 2.03). In MAR, the low oxygen fugacity was obtained for the rocks of Studen Kladenets (0.32 above the NNO buffer) and higher in Lozen (1.16–1.42) and Sheinovets (1.2–1.65, with two exceptions 0.13 and 0.88). All obtained data fall between HM and NNO buffers, closer to the second one, in the field of oxygen fugacity of the high-K and Ca-alkaline acid volcanics from the "orogenic belts" (Ewart 1979).

According to the amphibole hygrometer of Ridolfi et al. (2010) the water contents of the melt (Table 3) increase from the 2nd stage volcanics (average 3.30 wt.%) towards the 5th stage domes (average 3.85%), whereas the explosivity decrease. The higher water contents were calculated for the Borovitsa caldera border dyke (5.04%) and for the perlite from the Cherniya Kamak extracaldera dome (6.18%). In MAR, the calculated water contents are higher in Lozen and Sheinovets (average 4.36 and 4.94% respectively), but the highest value have been detected in one sample from the Studen Kladenets volcano (6.81%).

All lava rocks produced by water-rich melts are accompanied by large volume of water-bearing glass (perlite). It can be considered that these water contents of melts (between 2.7 and 6.8%) correspond to the so-called primary (magmatic) water in perlites. The opinion that the water in obsidians (up to 1%) can only be referred as primary (Perlites Genesis 1992 and references therein) has been widely accepted up to now. However, the quantity of water in some of the Eastern Rhodopean perlites (e.g. 5th stage domes in BR and Lozen volcano in MAR) is higher than calculated by the amphibole-based hygrometer. Therefore, they must have been additionally hydrated (Epel'baum et al. 1994) and oxidized, respectively, during their cooling at the surface. This might have resulted in formation of hematite nanoparticles in perlite glass (Calas et al. 1988; Dormann et al. 1989) giving its red-brown colour.

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