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PETROLOGICAL AND PETROCHEMICAL CHARACTERISTICS OF THE ROCKS OF THE KUSHLA CALDERA, EAST RHODOPE MASSIF

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Abstract: The Kushla caldera is located in the East Rhodope massif, in the border area of Bulgaria and Greece. The volcanic activity is realized during the Early Oligocene in subaerial environment. Several volcanic stages are distinguished: pre-caldera – dacite-trachydacite, latite and trachyte; syncaldera – acid pyroclastic rocks (mostly ignimbrites), and post caldera – elongated subvolcanic bodies and dykes of basaltic andesite and shoshonite. Different tendencies of magmatic evolution are found which is probably related to magma differentiation in comparatively isolated core chambers that are settled at different level. Despite the fractional crystallization as the main process of magmatic differentiation for the separate tendencies, the processes of contamination and mixing are also important. The mixing is probably the triggering mechanism for the acid ignimbrite caldera-forming eruption. The magmatic evolution of the volcanic rocks of the Kushla and Ostren Volcanic Subcomplexes is due to fractionation of plagioclase, sanidine and in less extent of hornblende, biotite and pyroxene as well as the fluid factor that controls the P_2O_5, K_2O and Na_2O. The magmatic differentiation of the Gorski izvor and Uchkaya shoshonite is related to the fractionation of pyroxene, plagioclase, olivine, magnetite and apatite. The lower pressure of the hornblende from the acid pyroclastics of the Ostren Volcanic Subcomplex (1.4-1.9 kbar) supports the idea for the presence of shallow magmatic chamber after which empting the main caldera-forming eruption is realized. The pressure of the Chatalalmdere Volcanic Subcomplex is comparatively higher (2.2–2.6 kbar) which is in accordance with the later eruption of deeper levels of the same chamber.

Key words: Petrology, East Rhodopes, Kushla caldera

1. Introduction

Wide spread collision to post-collision magmatism that is connected to the collision of Apulia, a promontory of Africa, and the Pelagonium microplate of Eurasia has accomplished during the Paleogene in the FYROM-Rhodope-North Aegean Magmatic Belt. The volcanic activity is realized in subaqueous to subaerial environment and is accompanied by shallow marine and continental sedimentation. The petrological and petrochemical characteristics of the Kushla caldera, that is located in the East-Rhodope Volcanic Area – a part of this Tertiary magmatic belt, is the object of the present study.

2. Previous studies

The first geological and field mapping work in the area is made by Katskov, Shilyafov (1968). A detailed subdivision of the volcano-sedimentary succession is made by Yordanov, Kalinova (Sarov et al., 1997f). Most of the studies of rocks in the area are related mainly to separate petrological problems (Innocenti et al., 1984; Yanev, et. al., 1989; Elefteriadis, 1995; Lilov et. al., 2000). Elefteriadis (1995) in a general publication about the Oligocene volcanic rocks in Central Rhodope (North Greece) describes the Kotani-Kalotico volcanic area that is a continuation of the area studied in Greece. Petrological and geochemical study of the rocks of the Kushla caldera is made by Georgiev, Nedyalkov (Sarov et al., 2008).

3. Geological background and volcanological interpretation

The Kushla caldera (Fig. 1) is recently defined volcanic structure (Yordanov in: Sarov et al., 2008), that is located to the south of Zlatograd in the border area of Bulgaria and Greece. The volcanic activity is realized during the Early Oligocene in subaerial environment. Pre-caldera, caldera and postcaldera volcanic stages are distinguished. The volcanic and volcano-sedimentary succession is subdivided using mixed volcanological-lithostratigraphical principles (Yordanov et al. in: Sarov et al., 2008). The rocks of the pre-caldera, syn-caldera and post-caldera volcanic stages are assembled in the Sushitsa Volcanic Complex, which is subdivided in Volcanic Subcomplexes, formations and packages.

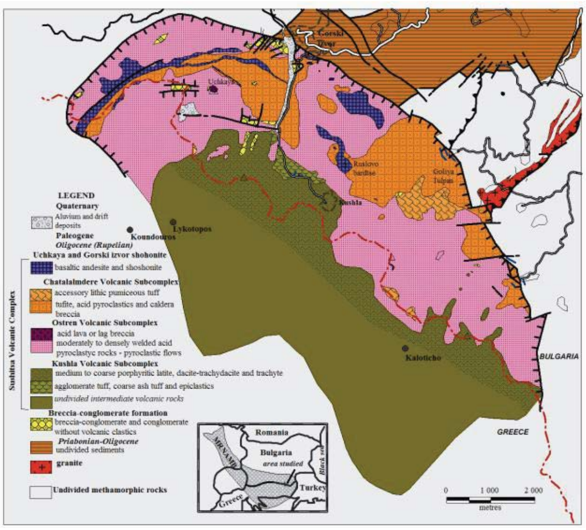

Fig. 1 Simplified geological map of the Kushla caldera. Compiled from the Geological map of Bulgaria in scale 1:50 000 (Sarov et al., 2008) and the geological scheme of Elefteriadis (1995) with additions. The contour of the FYROM – Rhodope – North Aegean magmatic belt (MRNAMB) is after Marchev et al. (2002).

Before the beginning of the volcanic activity the Gorski izvor depression is formed. It is filled with sandstone and conglomerate without volcanic clastics. The pre-caldera volcanic activity is related from latite to dacite-trachydacite and trachyte rocks of the Kushla Volcanic Subcomplex. It is overlied by a thick succession of moderately to densely welded pyroclastic rocks that are a product of powerful eruption of pumiceous pyroclastic flows (ignimbrites) of the Ostren Volcanic Subcomplex. During this eruption the main caldera collapse is established. Large boulders (up to 100 m^3) of sandstone and breccia-conglomerate (without volcanic clastics) as well as smaller fragments of intermediate volcanic rocks and metamorphic rocks are included in the ignimbrites during the eruption. The presence of carbonified wood remains in the pyroclstics defines that the volcanic activity is in subaerial environment. At the end of the pyroclastic activity, the comparatively poorer of fluids magma is intruded as rhyolitic lava breccia or lag breccia and the Uchkaya volcanic centre is formed. After that, along the caldera faults, basaltic andesite and shoshonite bodies and dykes (Gorski izvor shoshonite) are intruded. The erupted acid magma chamber free space (the lithostatic pressure is low) for the resurgent intrusion of the deeper situated more basic magma. After that follows a succession of acid pyroclastic rocks in alternation with tuffite and sandstone (Chatalalmdere Volcanic Subcomplex). The acid volcanic activity continues but with changed characteristics and it is pursued with large rock collapses (caldera breccia is formed). Pumice accessory lithic tuffs that are a product of pumiceous mud flows are observed near to Goliya Tulpan summit. The presence of various by kind and size rock fragments of intermediate volcanic rocks, metamorphites, quartz, etc., as well as their concentration can be connected to a collapse of phreatomagmatic eruption column. Cored accretionary lapilli are observed in the pyroclastic layers, evidence for water saturated eruption and deposition in subareial environment. A bed of fine ash-fall tuff that contains perfectly preserved plant remains (leaves and branches) is found. That defines its accumulation in subaerial or shallow lacustrine enviroment. The final resurgent stage is connected to the intrusion of basaltic andesite and shoshonite dykes and elongated bodies (Uchkaya shoshonite) along the caldera faults.

An interesting problem is the localization of the eruptive vents of the ignimbrites that have provoked the caldera subsidence. In the volcanology literature there are proposed different models for the eruptive vents of the caldera-forming ignimbrites but their localization is difficult to define and often under discussion. The characteristic for the ignimbrite of the Ostren Volcanic Subcomplex is that there is not prior Plinian phase that is related to the formation of ash-fall and base-surge pyroclastics. The ignimbrites are found only in the caldera. These, as well as the presence of the included disintegrated large boulders of breccia-conglomerate (up to 100 m^3) can lead to the conclusion that the caldera subsidence is accomplished during the ignimbrite eruption. The lack of prior Plinian ash-flow and base-surge phase defines that the vents are widened almost instantaneously. The convective column quickly collapsed and only pyroclastic flows formed. The high rate of the eruption caused the caldera roof subsidence around ring faults as is described for the Gran Canaria caldera (Soriano et al., 2006).

At the final stages of the formation of the rocks of the Ostren Volcanic Subcompex, the Uchkaya volcanic centre is formed. It is possible to be one of the eruptive vents that later is filled with rhyolitic lava breccia or lag breccia.

The vent of the pumiceous accessory lithic mud flow near to Peshterite place is located near to Golia Tulpan summit. The thickest deposits of the tuffs and also cavities primary filled with ankerite (now wholly altered in limonite) are observed there. This suggests intense hydrothermal (fumarolic) activity near the eruptive vent.

The Kushla caldera is imposed over metamorphic rocks and the sediments of the Kayaloba graben-brachy-syncline. The formation of the Gorski izvor monocline is a downsag that is connected with the caldera subsidence. The Kushla caldera is elliptically elongated in northwest-southeast direction, with long diameter of 12 km. According to the terminology of Lipman (1997) it is a combination between piece-meal, multicyclic and trap-door type.

There are few data for the absolute age of the volcanic rocks studied. According to K-Ar analyses of Innocenti et al. (1984) H-K andesite (Xerokori village) from the lowest parts of the section is 34 Ma and H-K basaltic andesite (Tsalapetinos village) – 25 Ma. The K-Ar ages of the shoshonite to the south-east of Gorski izvor village (Lilov et al., 2000) are in the range of 31,21–32,11 Ma (± 1,26 Ma).

4. Methods

Geological field study is made on Bulgarian territory during which the different rock varieties are sampled. The rock samples are analysed for the major oxides using ICP in the Central Scienceinvestigation laboratory “Geochemistry” of the Mining and Geology University “St. Ivan Rilski”. The trace and rare-earth elements are analyzed with ICP in the “Geolab” laboratory of BAS. 102 microprobe analyses of the main porphyries of the volcanic rocks are made with Jeol JSM 35CF at gathering the spectra for 100 sec at 20 KW. For more complete characterization of the rocks, analyses from previous studies are also used.

5. Results and Discussion

5.1. Petrographical characteristics

The volcanic rocks that build up the Sushitsa Volcanic Complex have a variety petrographical characteristics. Basic to intermediate and acid rocks that build lava and subvolcanic bodies as well as pyroclastic and epiclastic rocks are found.

The rocks of the ***Kushla Volcanic Subcomplex*** are presented by intermediate pyroclastics (agglomerate tuff and coarse ash tuff), epiclasics and lava rocks. The lava rocks are brown-violet, massive, medium to coarse plagioclase and sanidine-phyric latite, trachyte and dacite-trachydacite (Fig. 2a). The structure is porphyric, glomeroporphyric and trachytic. The primary minerals constitute 10–30 % of the rock volume. They are presented by plagioclase, sanidine, biotite, clinopyroxene, hornblende and quartz. The plagioclases (oligoclase) are weakly zonal with inclusions of apatite and recrystallized volcanic glass. Some of the larger porphyritic crystals have a periphery of sanidine (Fig. 2b). Carlsbad and albite twinings are observed. The sanidine is in comparatively subordinate or an equal quantity with the plagioclase. It is often clayey and sericitized. The quartz is rare with characteristic bay-like shapes that define processes of magmatic corrosion (Fig. 2c). The accessory minerals are zircon and apatite. The matrix is hyalopilitic, with subparallel microlites of plagioclase, sanidine and apatite, crystallites and ore minerals.

The ***Ostren Volcanic Subcomplex*** consists mainly of rhyolitic to trachyrhyolitic pyroclastic rocks (ignimbrite) formed by successive pyroclastic flows (Fig 2d). The rocks are white-grey, pinkish or greenish coloured. They consist of crystaloclasts, pumice (fiamme), lithoclasts and matrix. The crystaloclasts build 3–50 % from the rock volume. In most cases they are unsorted, various by size and often cataclastically deformed. The salic minerals prevail over the mafic. They are presented by quartz, plagioclase (oligoclase, andesine, labrador), sanidine (in comparatively equal quantity with the plagioclase), biotite and rarely hornblende and pyroxene. The welding rank of the pyroclastics, according to the classification of Quane and Russell (2004) is IV-VI rank or according to the classification of Steck and Grunder (1995) from partially welded with fiamme to densely welded. This means that the deformation of the pumice is from moderate to presence of eutaxitic texture and collapse to fiamme and even to forming of vitrophyre. The fiammes (Fig 2e) are differently coloured, hardly elongated and flattened (1–10 cm), sometimes with irregular contours or porous. In some cases they are bent and deformed that shows processes of post depositional rheomorphic flowage. Because of the denser welding, sometimes the fiammes are coalescence with the matrix. In most cases they are devitrified at different extent to fibrous and micrograined aggregate and spherulites (Fig. 2f) probably of K-feldspar and quartz.

Vitrophyre of molten pyroclastics, which partly intersect the ignimbrite is observed near to Ostra chuka summit. The rocks are massive with fluidal, vitrophyre and crystallite texture. It consists of matrix of brownish perlite and many elongated lense-like fragments of black coloured perlite (0.5–5 cm) identical with fiamme (Fig. 2g). These perlite varieties are also microscopically distinguishable.

The matrix of the brownish perlite (Fig. 2h) is devitrified to clayey minerals, smectites and zeolites.

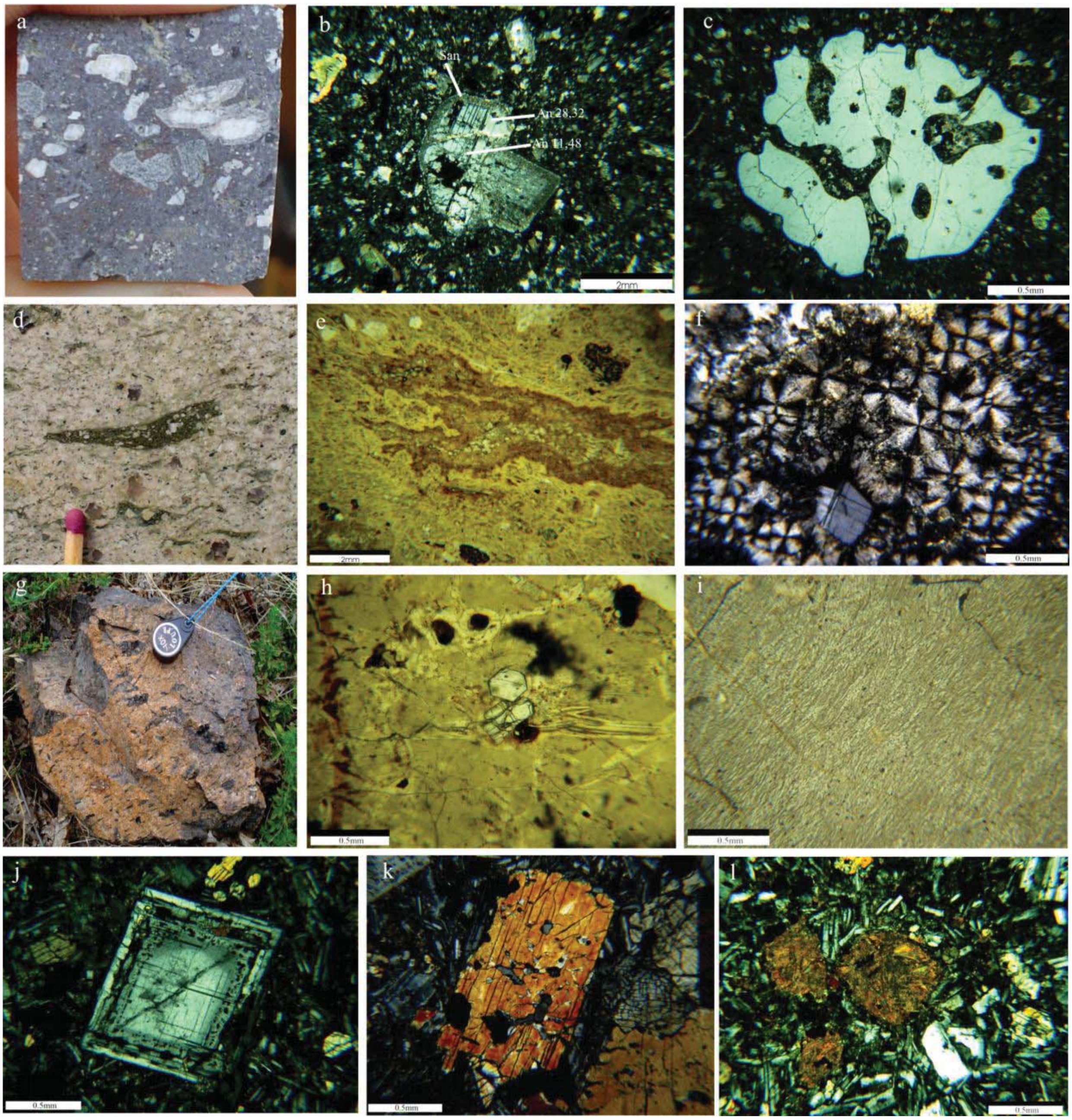

Fig. 2 Petrographic features of the volcanic rocks of the Kushla caldera: Kushla Volcaic Subcomplex a) coarse plagioclase- and sanidine-phyric trachydacite, the plagioclase is with sanidine periphery; b) microscopic view of the same as (a) – the plagioclase is with reverse zoning; c) magmatically corroded quartz; Ostren Volcanic Subcomplex d) densely welded tuff with fiamme; e) fiamme texture; f) devitrified fiamme to spherulites of Kfeldspar and quartz; g) vitrophyre; h) groundmass of brownish perlite; i) fiamme-like lenses of crystallites – longulites; Uchkaya shoshonite j) bitovnite with skeleton periphery; k) clynopyroxene; l) wholly altered olivine.

It has porphyries of plagioclase (andesine), sanidine, biotite, quartz, clinopyroxene and accessory minerals of apatite, titanite and ore minerals. The macroscopically black perlite (the fiamme-like) is grey coloured microscopically, non-altered, with fluidal texture and crystallites of the type of longulites (Fig. 2i). The porphyries in it are very rare and are represented by plagioclase and biotite.

The Chatalalmdere Volcanic Subcomplex consists of chaotic coarse terrigenous, tuffaceous sediments and acid pyroclastic rocks. Massive porous acid accessory lithic pyroclastic rocks expose near to the Peshterite place and Goliya Tulpan summit. A specific feature is the numerous cavities (1–50 cm) that in most cases are horizontally flattened parallel to the deposition surfaces. The cavities are formed due to gas vesicles or eroded pumices. The accessory and incidental lithic fragments are presented by variegated rock fragments of volcanic and metamorphic rocks, from mm to over 1m in size. The pumice is colourless, intensely to wholly altered with erased morphology. It is devitrified to cryptocrystalline aggregate of quartz and K-feldspar. The crystaloclasts are plagioclase (oligoclase – andesine), sanidine, biotite and quartz.

The Gorski izvor and Uchkaya basaltic andesite and shoshonite have comparatively similar petrographical and petrochemical characteristics. They are massive, dark green to black coloured. The primary minerals are plagioclase (andesine, labrodor to bitovnite), clinopyroxene, orthopyroxene and sometimes olivine. They consist 5–15% of the whole rock volume. The plagioclases (50–65% from the porphyries) often have skeleton periphery and are partly altered into carbonate and sericite (Fig. 2j). Oscillatory zonation is observed. The accessory minerals are apatite and magnetite. The clinopyroxene (Fig. 2k) is augite and the orthopyroxene is enstatite. The olivine (Fig. 2l) in most cases is altered in smectite, chlorite, serpentine and numerous ore minerals. The matrix is with microlite, interstitial, sometimes with wholly crystalline fine-grained microdolerite texture. It consists of numerous parallel oriented to intersertal plagioclase microlites and ore grains. The space between them is filled with brown, partly smectitized volcanic glass.

5.2. Comparative analysis of the rock-forming minerals

For better understanding the characteristics of the porphyries (and crystaloclasts) in the volcanic rocks, microprobe analyses are made (Table 1, 2, 3, 4).

The plagioclases composition (Fig 3a) of the rocks of the Kushla Volcanic Subcomplex varies from acid oligoclase to oligoclase-andesine. Reverse zoning is observed in some of the larger cryststals. The plagioclases from the acid pyroclastic rocks of the Ostren Volcanic Subcomplex are more basic than those in the Kusla Volcanic Subcomplex. Their composition varies in wide range – from oligoclase, andesine (predominantly) to even labrador. Zonation in the separate crystals is not observed. The difference in the composition of the separate plagioclase porphyries is a sign for mixing processes. The more acid composition of the plagioclases in the trachydacite of the Kushla Volcanic Subcomplex in relation to that in the more acid pyroclastic rocks of the Ostren Volcanic Subcomplex is probably due to inclusion of the Ca in the earlier crystallized mafic minerals while in the Ostren that is weakly pronounced.

The plagioclases in the Gorski izvor shoshonites are labrador, while in the Uchkaya instead of labrador, bitnovnite is also observed.

The composition of the sanidine of the trachydacite of the Kushla Volcanic Subcomplex varies in wide range – from comparatively rich in orthoclase component to almost pure anorthoclase. The sanidines of the acid pyroclastics of the Ostren Volcanic Subcomplex have comparatively rich orthoclase component.

All of the analyses of clynopyroxenes (Fig 3b) fall in the field of the augite. The orthopyroxenes of the Uchkaya shoshonite are enstatite.

Most of the hornblende crystaloclasts of the Ostren Volcanic Subcomplex are magnesiohornblende (Fig 3c). In some of them the core is edenite and the periphery is magnesio-hornblende. All of the hornblendes in the pyroclastics of the Chatalalmdere Volcanic Subcomplex are ednite (Fig 3d).

Analyses of unaltered biotites (Fig 3e) are made only from the vitrophyre of the Ostren Volcanic Subcomplex and they are of siderophylite-eastonite order. On the discrimination diagram for biotites (Abdel-Rahman, 1994) the analyses fall in the field of the calcium-alkaline orogenic suits (Fig 3f).

5.3. Petrochemical characteristics

The Sushitsa Volcanic Complex consists of volcanic rocks with intermediate to acid composition (Table 5, 6). The analyses of the rocks of the Kushla Volcanic Subcomplex fall in the fields of latite, dacite to trachydacite and trachyte (Fig 4). The trachyte is determined on the basis of the low composition of normative quartz (13.53 %) after CIPW calculation. The pyroclastic rocks of the Ostren Volcanic Subcomplex have composition of rhyolite and trachyrhyolite. Upper in the succession of the pyroclastics a weakly pronounced tendency of SiO_2 decreasing is observed which shows the eruption of weakly zoned magma chamber. The Gorski izvor and Uchakaya shoshonites have comparatively simiral petrochemical characteristics. The analyses fall in the fields of basaltic andesite and shoshonite, some of them at the border with andesite. Nevertheless their whole rock chemical composition some of the rocks have petrographical features of basalt.

Uchkaya shoshonite (samples Y, 7470a, 7484) have normative olivine.

The dependence between the major oxides and SiO_2 is presented on Harker diagrams (Fig. 6). Different tendencies of magmatic evolution are clearly distinguishable. One of the tendencies is connected to the Uchkaya and Goski izvor shoshonites and the other to the volcanic rocks of Kushla and Ostren Volcanic Subcomplex. According to Al_2O_3, TiO_2, CaO, Fe_2O_{3tot}, MgO and P_2O_5 for the both groups decreasing of the contents with increasing of SiO_2 is observed. The two trends are situated with retreat one to another or show different slopes, that correspond to different dynamics in their petrochemical evolution. According to K_2O the analyses of Gorski izvor and Uchakaya shoshonite fall in one field at similar SiO_2 contents, while for the Kushla and Ostren Volcanic Subcomplexes a decreasing with increasing of SiO_2 content is observed. In most cases the analyses from the Kushla and Ostren Volcanic Subcomplexes form separate trends that are subparallel oriented or an eshelon one to another. These features are clear for the K_2O, Na_2O and CaO and weakly pronounced for the Al_2O_3. For the P_2O_5 and MgO the trends have same tendencies but different slopes. For the TiO_2 and Fe_2O_{3tot} the trend is general.

Table. 1 Representative microprobe analyses of feldspar from the rocks of the Sushitsa Volcanic Complex: Ku - Kushla Volcanic Subcomplex, Os - Ostren Volcanic Subcomplex, G-Gorski izvor shoshonite, Ch-Chatalalmdere Volcanic Subcomplex, U-Uchkaya shoshonite.

	Ku	Ku	Ku	Ku	Ku	Os	Os	Os	Os	Os	G	Os	Ch	Ch	Ch	U	U
	san	san	san	Pl	Pl	san	san	Pl	Pl	Pl	Pl	Pl	san	san	Pl	Pl	Pl
N	3373	3373	3373	3373	3373	3240	3238	3240	3240	3238	2182A	3238	3244	3244	3244	3402A	3389A
				core	rime					rime	core					micr	core
SiO_2	63,56	65,12	71,70	63,88	59,97	65,62	65,03	60,73	59,71	60,92	54,12	61,18	63,57	63,79	59,34	52,04	48,01
TiO_2	0,14	0,10	0,09	0,00	0,00	0,27	0,13	0,08	0,00	0,00	0,10	0,05	0,53	0,00	0,00	0,00	0,00
Al_2O_3	19,61	20,37	15,32	22,13	24,76	18,98	18,77	25,03	26,26	25,29	28,08	24,23	20,78	20,27	25,67	30,55	33,28
FeO	0,44	0,88	1,72	0,08	0,51	0,00	0,14	0,16	0,36	0,16	0,60	0,21	0,15	0,21	0,33	1,23	0,39
MnO	0,00	0,00	0,00	0,00	0,10	0,27	0,00	0,00	0,00	0,00	0,00	0,00	0,16	0,00	0,00	0,00	0,00
MgO	0,62	0,54	0,35	0,00	0,25	0,00	0,29	0,84	0,52	0,00	0,78	0,30	0,68	1,07	0,78	0,47	0,46
CaO	0,00	0,92	0,26	2,45	5,93	0,26	0,00	6,74	7,81	6,07	10,65	5,61	0,44	0,11	6,07	12,60	15,57
Na_2O	2,60	6,23	3,25	10,17	7,74	1,66	3,22	5,09	4,78	6,21	4,70	7,27	2,04	3,07	6,87	3,19	1,78
K_2O	12,39	5,98	7,16	0,41	0,84	13,11	12,43	0,55	0,92	1,08	0,53	1,00	11,75	11,50	0,94	0,50	0,00
Tot	99,40	100,10	99,90	99,65	100,14	100,21	100,02	99,26	100,39	99,77	99,60	99,88	100,13	100,60	100,02	100,61	99,51
Si	11,786	11,719	12,753	11,38	10,75	11,996	11,932	10,90	10,63	10,84	9,91	10,93	11,695	11,730	10,66	9,46	8,85
Al	4,285	4,320	3,211	4,64	5,23	4,089	4,059	5,29	5,51	5,30	6,06	5,10	4,505	4,393	5,44	6,55	7,23
Fe(ii)	0,068	0,132	0,256	0,01	0,08	0,000	0,021	0,02	0,05	0,02	0,09	0,03	0,023	0,032	0,05	0,19	0,06
Ca	0,000	0,177	0,050	0,47	1,14	0,051	0,000	1,30	1,49	1,16	2,09	1,07	0,087	0,022	1,17	2,45	3,08
Na	0,935	2,173	1,121	3,51	2,69	0,588	1,145	1,77	1,65	2,14	1,67	2,52	0,728	1,094	2,39	1,12	0,64
K	2,931	1,373	1,624	0,09	0,19	3,057	2,909	0,13	0,21	0,25	0,12	0,23	2,757	2,698	0,22	0,12	0,00
Tot	20,004	19,895	19,014	20,10	20,08	19,782	20,066	19,41	19,54	19,71	19,95	19,89	19,795	19,969	19,92	19,89	19,85
An	0,00	4,76	1,77	11,48	28,32	1,38	0,00	40,59	65,65	32,65	53,83	28,11	2,43	0,57	30,94	66,43	82,86
Ab	24,18	58,37	40,10	86,23	66,90	15,92	28,25	55,47	34,02	60,44	42,99	65,92	20,37	28,70	63,36	30,43	17,14
Or	75,82	36,87	58,13	2,29	4,78	82,71	71,75	3,94	0,33	6,92	3,19	5,97	77,20	70,73	5,70	3,14	0,00

In most of the volcanic rocks of the Sushitsa Volcanic Complex the content of K_2O is higher than that of Na_2O, and even in the cases when the N_2O is prevailing the rocks are still in the potassium series. Most of the rocks are high potassium but some of them are at the border with the medium potassium (Fig. 5).

According to the normative mineral composition, calculated using CIPW, most of the volcanic rocks are Si oversaturated but some of the analyses of the

Table. 2 Representative microprobe analyses of clinopyroxene from the rocks of the Sushitsa Volcanic Complex (abbreviations as Table 1).

	Os	G	G	Ch	U	U	U	U
N	3240	2182A	2182A	3244	3402A	3402A	3402A	3389A
loc		rime	core		micr	core	rime	core
SiO_2	52,39	49,27	52,32	51,92	52,12	50,76	50,86	51,80
TiO_2	0,00	0,44	0,49	0,05	0,67	0,68	0,62	0,30
Al_2O_3	2,21	4,86	4,20	2,12	4,27	4,67	4,64	4,79
Cr_2O_3	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
FeO	8,97	8,84	7,60	8,03	11,63	10,95	8,73	6,96
MnO	1,13	0,51	0,19	0,68	0,30	0,23	0,31	0,30
MgO	14,54	15,09	15,07	14,69	12,26	14,27	14,82	15,94
CaO	20,65	20,10	20,44	20,02	16,54	16,66	19,86	19,68
Na_2O	0,00	0,61	0,00	1,85	0,95	1,07	0,00	0,00
K_2O	0,00	0,00	0,00	0,00	0,94	0,54	0,00	0,06
Tot	99,91	99,73	100,33	99,40	99,72	99,86	99,87	99,87
Si	1,95	1,84	1,92	1,95	1,95	1,90	1,89	1,90
Al	0,05	0,16	0,08	0,05	0,05	0,10	0,11	0,10
T	2,00	2,00	2,00	2,00	2,00	2,00	2,00	2,00
Al	0,05	0,06	0,10	0,04	0,14	0,10	0,09	0,11
Fe^{3+}	0,00	0,17	0,00	0,22	0,00	0,10	0,00	0,00
Mg	0,81	0,76	0,82	0,74	0,48	0,78	0,82	0,87
Fe^{2+}	0,14	0,00	0,06	0,00	0,36	0,00	0,07	0,01
Ti	0,00	0,01	0,01	0,00	0,02	0,02	0,02	0,01
M1	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00
Fe^{2+}	0,14	0,10	0,17	0,03	0,21	0,24	0,20	0,20
Mn	0,04	0,02	0,01	0,02	0,01	0,01	0,01	0,01
Mg	0,00	0,09	0,00	0,08	0,00	0,02	0,00	
Ca	0,82	0,81	0,80	0,80	0,66	0,67	0,79	0,77
Na	0,00	0,04	0,00	0,13	0,07	0,08	0,00	0,00
K	0,00	0,00	0,00	0,00	0,04	0,03	0,00	0,00
Wo	42,33	40,68	43,01	39,64	37,04	35,36	41,77	41,39
En	41,48	42,50	44,13	40,48	38,21	42,15	43,37	46,65
Fs	16,19	14,58	12,87	13,25	20,90	18,37	14,86	11,96

The chondrite-normalized spidergrams of Gorski izvor and Uchkaya shoshonite (Fig 7a) have similar pattern and characteristics of calcium alkaline basalts of destructive plate boundaries. Comparatively high contents (sometimes over 10 times more) of the heavy REE in comparison to that in the chondrite and weak Eu anomalies are observed (Fig 7b). On the Ti/Zr diagram the analyses fall in the field of the calcium alkaline basalts (Fig 7c). The ORG-normalized spidergrams (Fig 8a) of the pyroclastic rocks of the Ostren and the trachydacite of the Kushla Volcanic Subcomplex show high concentration of LILE (K, Rb, Ba, Th) and decreasing of HFSE (Nb, Hf, Zr, Sm, Y, Yb). This configuration is typical for the syn- to postcollision granites of Pearce et al. (1984). Characteristic are the high positive Rb anomalies of the pyroclastic rocks of the Ostren Volcanic Subcomplex but positive Th and negative Ba anomalies are not observed. On its left part the pattern of the trachydacite of Kushla Volcanic Subcompex resemble the intraplate granite from Oman. Weak Eu anomalies are observed (Fig 8b). On the (Y+Nb) – Rb diagram (Fig. 8c) the analyses of the acid pyroclastics of the Ostren Volcanic Subcomplex fall in the field of the syncollision granite and that of the trachydacite of Kushla Volcanic Subcomplex – in the field of the volcanic arc granite.

Table 3. Representative microprobe analyses of orthopyroxene from the rocks of the Sushitsa Volcanic Complex (abbreviat. as Table 1).

	U	
N	3389A	3389A
loc	core	rime
SiO_2	50,97	51,18
TiO_2	0,07	0,23
Al_2O_3	1,65	1,78
FeO	20,96	19,46
MnO	0,81	0,93
MgO	23,47	24,03
CaO	1,39	1,82
Na_2O	0	0
K_2O	0,19	0,22
Tot	99,54	99,68
Si	1,914	1,909
Al	0,073	0,078
Fe(iii)	0,013	0,012
Tot	2,000	2,000
Al	0,000	0,000
Fe(iii)	0,141	0,137
Ti	0,002	0,006
Mg	1,314	1,337
Mn	0,026	0,451
Fe(ii)	0,496	0,029
T	1,978	1,960
Ca	0,056	0,073
Na	0,000	0,000
K	0,009	0,010
Wo	2,73	3,57
En	64,24	65,57
Fs	33,03	30,86

Table 4. Representative microprobe analyses of hornblende from the rocks of the Sushitsa Volcanic Complex (abbreviat. as Table 1).

	Os	Os	Os	Ch	Ch
N	3240	3238	3238	3244	3244
loc		core	rime		
SiO_2	49,25	49,51	48,06	46,24	47,37
TiO_2	0,97	0,74	0,81	0,80	0,75
Al_2O_3	7,27	6,26	7,20	8,43	7,91
FeO	14,37	12,69	13,32	12,92	12,02
MnO	0,85	0,88	0,89	0,57	0,44
MgO	15,41	15,63	15,31	14,50	15,05
CaO	11,04	10,96	10,92	10,68	10,36
Na_2O	0,00	0,86	1,40	3,13	3,71
K_2O	0,82	0,64	0,80	0,77	0,62
Tot	100,0	98,2	98,7	98,1	98,3
Si	6,96	7,15	6,96	6,80	6,90
Al(iv)	1,04	0,85	1,04	1,20	1,10
T	8,00	8,00	8,00	8,00	8,00
Al(vi)	0,18	0,22	0,19	0,26	0,26
Ti	0,10	0,08	0,09	0,09	0,08
Cr	0,00	0,00	0,00	0,00	0,00
Fe(iii)	0,51	0,11	0,13	0,00	0,00
Fe(ii)	1,19	1,42	1,48	1,59	1,46
Mn	0,10	0,11	0,11	0,07	0,05
Mg	2,92	3,06	3,00	2,99	3,14
C	5,00	5,00	5,00	5,00	5,00
Mg	0,33	0,30	0,31	0,18	0,14
Ca	1,67	1,70	1,69	1,68	1,62
Na	0,00	0,00	0,00	0,14	0,25
B	2,00	2,00	2,00	2,00	2,00
Na	0,00	0,24	0,39	0,76	0,80
K	0,15	0,12	0,15	0,14	0,12
A	0,15	0,36	0,54	1,04	1,16

The fractionation of REE (the attitude La_n/Yb_n) is most significant for the rocks of Kushla Volcanic Subcomplex and for the acid pyroclastic rocks (Ostren Volcanic Subcomplex) from the higher part of the succession. The fractionation of heavy REE is weakest for the Ostren Volcanic Subcomplex, where the attitude Eu_n/Yb_n is close to one and this probably is due to that the participation of femic minerals (pyroxene and hornblende) during the process of fractionation is weak.

Table. 5 Major element data from the rocks of Sushitsa Volcanic Complex

	Kushla Volcanic Subcomplex					Ostren Volcanic Subcomplex						G		Ch			Uchkaya shoshonite				
№	1107	1119Б	3372Г	3196	3375Б	3237Б	3241Б	3198	3400Б	7506	3210	7476	2182Б	3209	3384Б	Y	3379Б	3402Б	3549Г	3197	3389Б
										2		2				1					
SiO2	59,6	64,5	64,7	66,9	68,6	70,12	72,1	72,4	72,6	74,5	52,4	52,9	55,6	71	73	51,2	52,4	52,4	54	55,7	56,9
TiO2	0,74	0,45	0,46	0,61	0,43	0,43	0,21	0,33	0,32	0,28	1,08	1,01	1,03	0,28	0,09	0,51	1,04	1,13	1	1,19	0,92
Al_2O_3	14,6	16,4	15,8	16,8	15,1	15,06	13,5	13,8	13,4	12,6	18	17,9	16,8	13,2	13,7	17,9	17,4	17,5	17,2	17,1	16,1
Fe_2O_{3tot}	5,64	4,08	4,19	4,31	3,84	3,53	1,43	2,05	2,72	2,08	8,54	8,87	7,96	1,87	0,69	7,27	9,28	9,98	8,79	8,22	8,14
MnO	0,07	0,08	0,09	0,08	0,06	0,07	0,05	0,11	0,06	0,04	0,13	0,1	0,24	0,12	0,05	0,15	0,19	0,17	0,17	0,13	0,12
MgO	3,9	1,45	1,16	0,49	0,54	0,49	0,31	0,47	0,78	0,31	3,01	3,64	2,69	0,59	0,22	3,69	3,32	3,09	3,67	3,21	4,26
CaO	4,9	2,19	2,94	1,36	1,91	1,53	1,18	1,91	1,54	0,28	6,43	7,13	7,84	2,8	2,66	9,4	8,13	8,44	8,04	7,49	6,38
Na_2O	2,94	3,44	3,14	3,45	4,19	2,72	3	2,69	2,32	3,69	2,81	2,81	2,39	3,28	0,99	3,02	2,68	2,39	2,97	2,85	2,47
K_2O	5,72	5,95	4,32	3,6	4,08	4,96	4,57	3,38	4,16	3,61	2,45	3,13	1,99	2,85	4,16	2,38	3,2	1,83	2,54	2,25	2,81
P2O5		0,19	0,2	0,17	0,19	0,14		0,08	0,17		0,5		0,28	0,03	0	0,37	0,34	0,37	0,37	0,38	0,28
LOI	1,1	1,11	2,66	1,62	0,79	0,91	2,92	2,02	1,24	1,2	4,23	1,2	3,12	3,41	4,19		1,59	2,25	0,81	0,92	0,92
H_2O	0,72	1,06	2,07	0,93	0,67	1,16	1,84	0,41	1,15	0,31	0,56	1,15	1,24	1,11	2,32		1,11	1,38	1,66	0,75	1,83
Total	99,9	101	102	100	100	101,1	101	99,7	100	99	100	99,9	101	101	102	95,8	101	101	101	100	101

G - Gorski izvor shoshonite; Ch - Chatalalmdere Volcanic Subcomplex, 1. Yanev et al., 1989; 2. Sarov et al., 1997f.

Table. 6 Trace and rare-earth element data from the rocks of Sushitsa Volcanic Complex

	Ku		Os			G		U		
№	1119Б	3372Г	3237Б	3400Б	3198	3210	2182Б	3379Б	3389Б	3207
Sc	4,99	5,81	3,96	4,24	2,25	11,94	16,3	18,2	21,2	14,1
Cr	89	88,2				30	31,1	33,1	50,1	17
Co	5,02	15,1				17,04	15,3	20,1	19,2	17,3
Ni	7,11	6,03				6,2	6,04	10,1	11,1	4,02
Zr	77,3	66	34,1	41,4	27,8	140,1	119	112	126	11,3
Hf	2,02	1,73	0,89	0,9	1,03	2,85	2,63	2,39	2,56	2,44
Nb	9,27	12,8	12,6	12,6	14,1	10,4	9,27	6,18	6,18	10,4
Y	9,95	10,3	8,04	9,16	10,2	11,22	15,4	15,7	17,5	12,3
Th	15,4	12,8	14,4	17,3	15,2	4,21	5,33	3,79	6,06	
Rb	87,6	72	288	203	207	65,06	31,8	65,1	96,7	39,7
Sr	399	264	154	194	173	323,5	417	473	397	482
Ba	1408	925	1967	1684	1365	923	1694	1543	1069	2347
La	65,6	58,3	46	58,7	40,4	47,63	56,8	51,8	55,2	42,2
Ce	59,1	53,1	33,8	42	34,3	41,89	46,7	46,5	46,2	37,8
Sm	3,98	3,51	2,91	3,22	2,94	4,38	5,15	5,6	5,48	4,67
Eu	0,75	0,62	0,42	0,45	0,37	0,74	0,98	1,01	0,98	0,82
Yb	1,19	1,21	0,71	0,78	1,24	1,26	1,63	1,62	1,76	1,37

Ku - Kushla Volcanic Subcomplex; Os - Ostren Volcanic Subcomplex; G - Gorski izvor shoshonite; U - Uchkaya shoshonite.

5.4. Evaluation of the crystallization conditions

An attempt for evaluation of the thermo-barometric parameters of the crystallization process on the basis of the rock-forming mineral composition is made. For the acid pyroclastics of the Ostren Volcanic Subcomplex, using the hornblende geobarometre of Johnson and Rutherford (1989), pressure in the range of *1.4–1.9 kbar* is calculated. This corresponds to depth of crystallization of 4–6 km. The temperature of crystallization for the same rocks, using the hornblende-plagioclase equilibrium of Blundy and Holland (1990), is in the range of *725–760°C*. The same thermo-barometric methods are used for the acid pyroclastic rocks of the Chatalalmdere Volcanic Subcomplex. The evaluation results are as follow: pressure *2.2–2.6 kbar (6.5–8 km)* and temperature of *720–740 °C*.

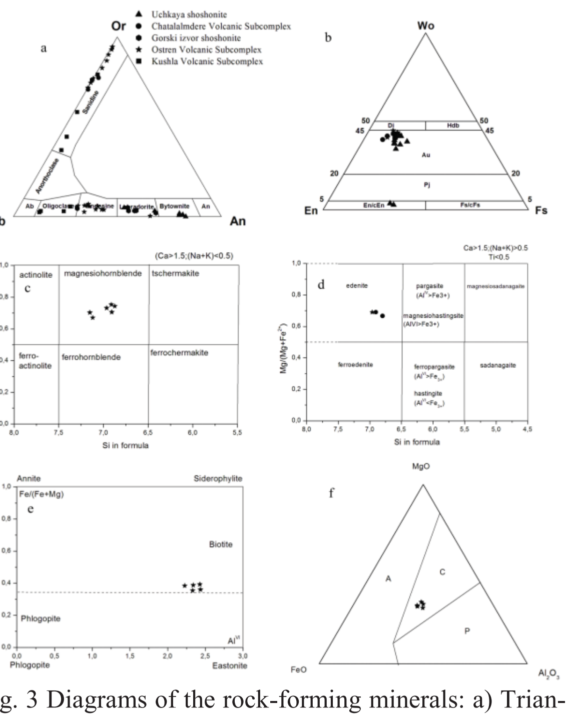

Fig. 3 Diagrams of the rock-forming minerals: a) Triangle diagram (Ab-An-Or); b)Triangle Diagram (Wo-En-Fs); c) Hornblende diagram (Bernard, 1997) - magnesio-hornblende; d) Hornblende diagram (Bernard, 1997) – edenite; e) Biotite diagram (Deer et al., 1966); f) Tectonic discrimination diagram $FeO–Al_2O_3–MgO$ (wt%) (Abdel-Rahman, 1994) of biotite composition, C – calcium alkaline orogenic suite.

The higher magnesium content of the hornblendes of the acid pyroclastics of the Chatalalmdere Volcanic Subcomplex (0.772–0.768) in comparison to the hornblendes of the acid pyroclastics of Ostren Volcanic Subcomplex (0,.9–1), can be connected to higher lithostatic pressure but lower H_2O– pressure and comparatively lower crystallization temperature.

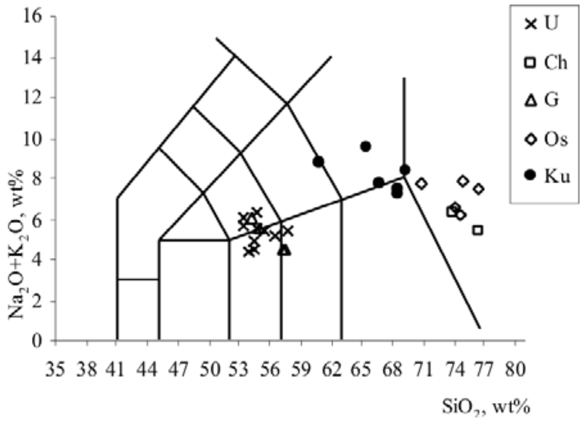

Fig. 4. TAS classification diagram (Le Bas et al., 1986) for the rocks of the Sushitsa Volcanic Complex: Ku – Kushla Volcanic Subcomplex; Os – Ostren Volcanic Subcomplex; G – Gorski izvor shoshonite. Ch – Chatalalmdere Volcanic Subcomplex; U – Uchkaya shoshonite.

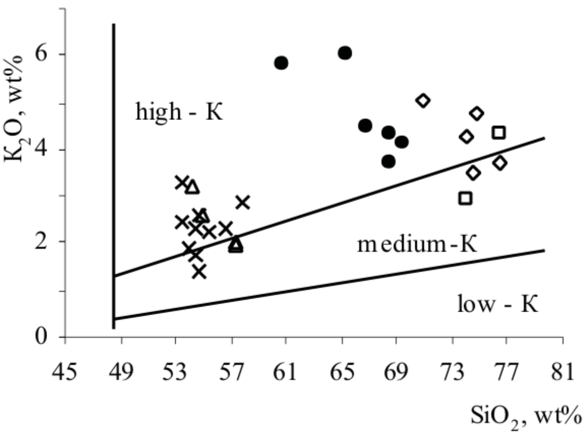

Fig. 5 SiO_2 versus K_2O diagram for the rocks of Sushitsa Volcanic Complex (Le Maitre et al., 1989) – signs as Fig. 4.

The crystallization temperature of the Uchkaya shoshonite, using the two-pyroxene geothermometre of Lindsley (1983), is in the range of 800-860^{o}C.

6. Conclusions

The Kushla caldera is located in East Rhodope massif, in the border area of Bulgaria and Greece. The volcanic activity is realized during the Early Oligocene in subaerial environment. Several general comparatively independent stages of the magmatic activity are distinguished. These are respectively the volcanic rocks of the precaldera (Kushla Volcanic Complex), syncaldera (Ostren and Chatalalmdere Volcanic Stbcomplexes) and the postcaldera resurgent stages (Gorski izvor and Uchakaya shoshonite). The volcanic and volcano-sedimentary rocks are combined in the Sushitsa Volcanic Complex (Yordanov et al., 2008). Basic to intermediate and acid volcanic rocks that build lava and subvolcanic bodies as well as pyroclastic (ignimbrite and ash-fall tuff) and epiclastic rocks are found. The volcanic rocks of the Kushla and

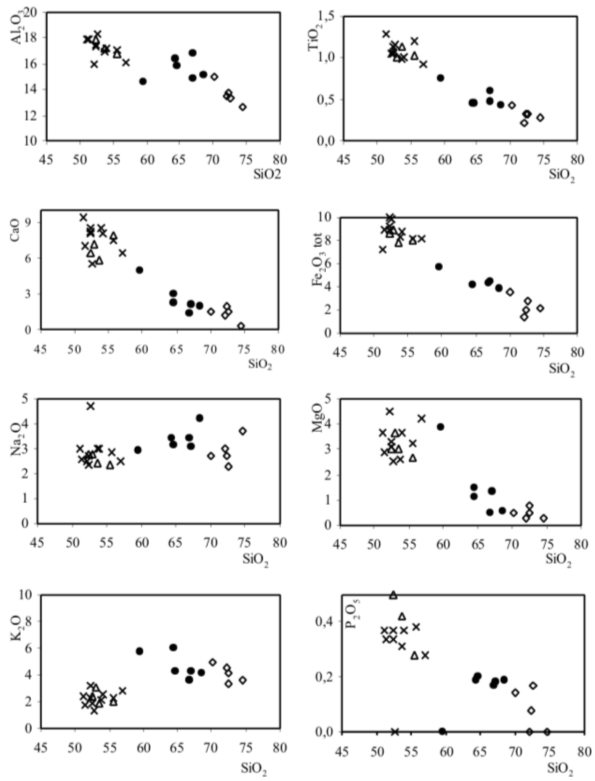

Fig. 6. Harker diagrams for the rocks of Sushitsa Volcanic Complex (Le Maitre et al., 1989) – signs as Fig. 4.

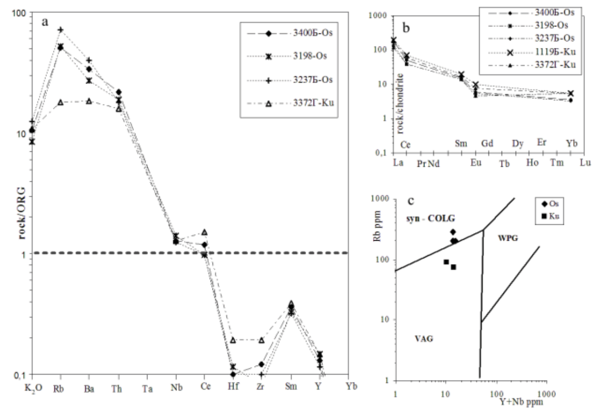

Fig. 7. a) Chondrite normalized spydergram of Gorski izvor and Uchkaya shoshonite, normalizing values after Thompson et al. (1984); b) Chondrite normalized REE pattern, normalizing values after Nakamura (1974): 7c) Discrimination diagram Ti/Zr (Pearce and Cann, 1973), C –calcium alkaline basalt.

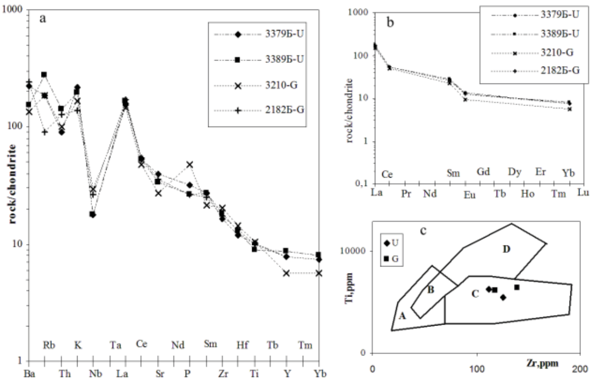

Fig. 8. a) ORG normalized spydergram, after Pearce et al. (1984), of the rocks of Kushla and Ostren Volcanic Subcomplexes; b) Chondrite normalized REE pattern, normalizing values after Nakamura (1974): 7c) Discrimination diagram Rb/(Y+Nb), after Pearce et al. (1984).

the Ostren Volcanic Subcomplexes, from the one hand and the Gorski izvor and Uchkaya shoshonite, from the other, have different way of magmatic evolution. This is probably related to magma differentiation in comparatively isolated core chambers that are settled at different level. The subparallel, an echelon situated one to another trends of the Kushla and Ostren Volcanic Subcomplexes is probably due to the formation of the rocks during two successive eruptive stages of shallow intermediate to acid magma chamber. The Gorski izvor and the Uchkaya shoshonite have the petrochemical features of comparatively independent magmatic evolution in one probably deeper setteled magmatic chamber. Despite the fractional crystallization as the main process of magmatic differentiation for the separate tendencies, the processes of contamination and mixing are also important. The mixing in the acid pyroclastic rocks of the Ostren Volcanic Subcomplex is defined by the various composition of the plagioclases (from andesine to labrador). This is the triggering mechanism for the ignimbrite caldera-forming eruption.

The magmatic evolution of the volcanic rocks of the Kushla and Ostren Volcanic Subcomplexes is due to fractionation of plagioclase, sanidine and at less extent of hornblende, biotite and pyroxene as well as the fluid factor that controls the P_2O_5, K_2O and Na_2O. The magmatic differentiation of the Gorski izvor and Uchkaya shoshonite is most likely to be connected to fractionation of pyroxene, plagioclase, olivine, magnetite and apatite. The lower pressure of the hornblende of the acid pyroclastics of the Ostren Volcanic Subcomplex (1.4-1.9 kbar) supports the idea for the presence of shallow magmatic chamber after which empting the main caldera-forming eruption is realized. The pressure of the Chatalalmdere Volcanic Subcomplex is comparatively higher (2.2–2.6 kbar) which is in accordance with the later eruption of deeper levels of the same chamber.

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