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Cs-bearing andesites in the volcanic region of Borovitsa, the Eastern Rhodopes

Yotzo Yanev, Peter Marchev, Raya Raicheva

Abstract. Cs content in interstitial glass and phenocrysts from Cs-bearing Paleogene intermediate rocks (a hyaloandesite dyke with Cs 152 ppm and a high-potassium andesite plug with Cs 143 ppm) is studied. Cs is concentrated in the groundmass glass of rhyolitic composition (an average of 360 and 760 ppm, respectively) and in some phenocrystal phases. These are orthopyroxene (an average of Cs 140 ppm) in high-potassium andesite and orthopyroxene (Cs 360 ppm), clinopyroxene (Cs 270 ppm), biotite (90 ppm), and some plagioclase phenocrysts (from 360 to 1300 ppm) in hyaloandesite. Cs is probably incorporated in the groundmass glass structure and plays the role of an ion-modifier. The high content of Cs in pyroxenes is probably dueto the heterovalent isomorphism of the following pattern: $Mg^{2+} + Fe^{2+} \rightarrow Cs^{+} + Fe^{3+}$.

Key words: Cs-andesites, Cs-pyroxenes, Paleogene collision volcanism, Eastern Rhodopes
Address: Y. Yanev, P. Marchev and R. Raicheva - Geological Institute, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria; E-mail: yotzo@geology.bas.bg

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Резюме. Изследвано е съдържанието на Cs в интерстициалното стъкло и в порфирите на Cs-съдържащите палеогенски среднобазични вулканити (хиалоандезитова дайка с Cs 152 ppm и висококалиев андезит с Cs 143 ppm). Cs е концентриран в стъклената основна маса с риолитов състав (средно 360 и 760 ppm съответно), както и в някои порфири. Това са ортопироксенът (средно Cs 140 ppm) във висококалиевия андезит и ортопироксенът (360 ppm), клинопироксенът (270 ppm), биотитът (90 ppm) и някои плагиоклазови фенокристали (от 300 до 1300 ppm) в хиалоандезита. Cs вероятно е включен в структурата на стъклото, където играе ролята на йон-модификатор. Високото му съдържание в пироксените е възможно да се дължи на хетеровалентен изоморфизъм по схемата $Mg^{2+} + Fe^{2+} \rightarrow Cs^{+} + Fe^{3+}$.

Ключови думи: Cs-андезити, Cs-пироксени, палеогенски колизионен вулканизъм, Източни Родопи
Адрес: Й. Янев, П. Марчев и Р. Райчева – Геологически институт, Българска академия на науките, София 1113

Introduction

Late Alpine (Priabonian-Oligocene) collision-related volcanism in the Eastern Rhodopes consists of large amounts of shoshonitic and high-potassium calc-alkaline lavas of predominantly acid and intermediate composition and subordinate basic varieties (Harkovska et al., 1989). In accordance with their K enrichment, the Eastern Rhodopes volcanics show elevated content of LIL elements and particularly of Cs. Values within the range of 2-35 ppm

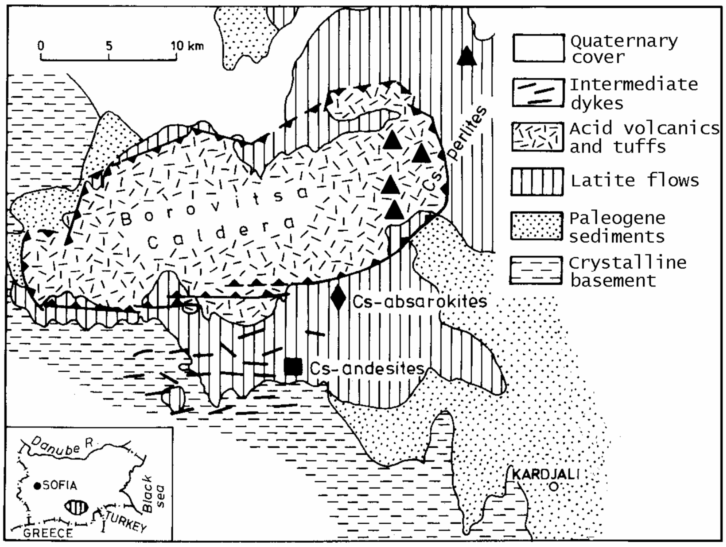

Fig. 1. Location map of the Eastern Rhodopes Cs-bearing volcanics
Фиг. 1. Схема на находищата на Източнородопските Cs-съдържащи вулканити

are the most typical for the whole range of rocks (Yanev, 1994a; Marchev et al., 1998). Along with this, a small number of glassy volcanic rocks show exceptionally high Cs contents. The highest values (up to 7400 ppm), which have been reported so far, are in trachyrhyolite perlites (Yanev, Karadjova, 1976; Yanev, 1994a), absarokites (an average of 300 ppm, Ivanov, Stoyanova, 1966; Yanev, 1994b), hialoandesites and latites (an average of 152 and 143 ppm, respectively, Marchev, 1979). Deposits of these volcanics are located in the periphery of the Borovitsa caldera in the Eastern Rhodopes area (Fig. 1), forming a NE-SW strip, parallel to the Dobromirtzy deep fault zone (Popov et al., 1972). However, similar Cs-bearing (140-340 ppm) glass-rich basalt and high-potassium andesite have recently been found also in the Oligocene Madjarovo volcano (Marchev et al., 1998, and unpublished data).

The purpose of this communication is to present detailed data on distribution of Cs in phenocrystal phases and groundmass glass of Cs-bearing intermediate volcanic rocks, established by Marchev (1979). Unlike the high-Cs acid rocks, Cs-bearing intermediate rocks are very rare. To our knowledge, this was the first finding of intermediate rocks with content of Cs > 100 ppm which was followed by several reports by Kremenetsky et al. (1980) for andesites and trachyandesites up to 90 ppm. High contents of Cs have been reported in slightly more basic volcanics - shoshonites from the Transbaikal region with Cs 146 ppm (Tauson et al., 1984) and basaltic andesite groundmass from Kozori, Sano district, Japan with 420 ppm (Hart, Brooks, 1974).

Location and petrography

The described Cs-bearing rocks form a tube-like body (plug) (sample 4) with a diameter of 15 m, and a dyke about 5 m thick (sample 4/1), located at a distance of 25-30 m from each other. They crop out 1 km northeast of the village of Russalsko, 20 km northwest of the town of Kardjali (Fig. 1). These bodies are an integral part of a large dyke swarm, located in the south edge of the Borovitsa volcanic region, which has been considered to be an important-magma-feeding structure at this part of the

Table 1. *Major elements (wt%), Cs content (ppm) and CIPW norms of the Cs-bearing andesites and interstitial glasses*

Таблица1. *Химически състав (тегл. %), съдържание на Cs (ppm) и CIPW нормативен състав на изследваните Cs-съдържащи андезити и техните интерстициални стъкла*

Vol-canics	High-K andesite	Hyalo-andesite	High-K andesite glass	Hyalo-andesite glass
Samples	4/1	4	4/1	4
			n=11	n=19
SiO_2	59.60	58.18	75.23	77.42
TiO_2	0.69	0.69	0.33	0.45
Al_2O_3	15.68	15.78	14.38	14.57
Fe_2O_3	2.48	2.34	-	-
FeO	2.40	2.14	1.12_{total}	0.42_{total}
MnO	0.10	0.09	0.02	0.02
MgO	3.16	2.83	0.27	0.07
CaO	6.27	6.75	2.53	4.43
Na_2O	2.93	3.71	2.96	1.84
K_2O	3.15	1.51	3.18	0.78
P_2O_5	0.34	0.17	n.d	n.d
H_2O^-	0.76	1.85	n.d	n.d
H_2O^+	1.86	3.51	n.d	n.d
Total	99.42	99.55	100.00	100.00
Na_2O/K_2O	0.93	2.46	0.93	2.36
Cs (ppm)	143	152	760	363
Q	14.53	14.41	39.68	54.80
Or	18.62	8.92	18.97	4.61
Ab	24.79	31.39	24.87	15.57
An	10.33	21.95	12.50	21.98
C			1.45	2.65
Di	6.77	8.24		
Hy	6.06	4.18	2.27	0.23
is			0.68	0.85
Mt	3.60	3.39		
Il	1.32	1.32		
Ap	0.81	0.40		

n - number of analyzed samples

n – брой на анализите

region (Ivanov, 1972; Marchev, 1985).

Petrographically, the Cs-bearing rocks studied are defined as latite (sample 4/1) and hyaloandesite (sample 4) by Marchev. However, unlike the K_2O/Na_2O ratio of sample 4/1 (1,07 - Table 1), it falls within the field of high-potassium andesites on the diagram of Peccerillo and Taylor (1976) (Fig. 2). The two rocks are strongly porphyritic comprised by phenocrysts (45-48%) of zoned plagioclase, ortho- and clinopyroxene, rarely amphibole and biotite and accessories of apatite and Ti-magnetite. Average and representative microprobe analyses on phenocrysts are given in Tables 2 and 3. Plagioclase in the high-potassium andesite is normally zoned andesine with an $An_{46-48}Or_{5-6}$ core and an outer zone of $An_{37}Or_{7-10}$, whereas hyaloandesite plagioclases have a more anortite-rich core ($An_{38-62}Or_{2-7}$) and an outer zone ($An_{39-47}Or_{6-10}$). Outer zones of plagioclase in both rocks show considerable increase of potassium and it can be classified as K-andesine. Orthopyroxene in both rocks is enstatite of similar composition: $Wo_{2,7}En_{69,5}$ in the high-potassium andesite and $Wo_{2,4}En_{68}$ in the hyaloandesite. Clinopyroxene is augite ($Wo_{43}En_{44,3}$ and $Wo_{44}En_{43,5}$, respectively) with rare Mg-richer cores ($Wo_{41}En_{49}$). Biotite is an intermediate between annite and phlogopite ($Mg^{\#}$68, ^{IV}Al 2,43-2,44) whereas amphibole is pargacite with higher $Mg^{\#}$ (73). The two rocks differ essentially in groundmass textures. The high-potassium andesite shows a pilotaxitic texture, wich consists of feldspar and pyroxene microlites and a small amount of glass. The hyaloandesite texture is vitrophyric with perlite cracks and a small amount of feldspar microlites and pyroxene crystallites. The glass composition of both rocks (Table 1, Fig. 2) is rhyolitic ($Q_{40}Or_{19}Ab_{25}$ and $Q_{54}Or_5Ab_{17}$) with Na_2O/K_2O ratios similar to those for the bulk rock.

Analytical methods and content of Cs

Cesium in the bulk rock was analyzed by flame photometric analyses (Marchev, 1979). Quantitative analyses of groundmass and phenocrysts composition, including contents of Cs were carried out using WDS system under standard conditions with a Camebax microprobe at the University of Paris *VI* and *VII*.

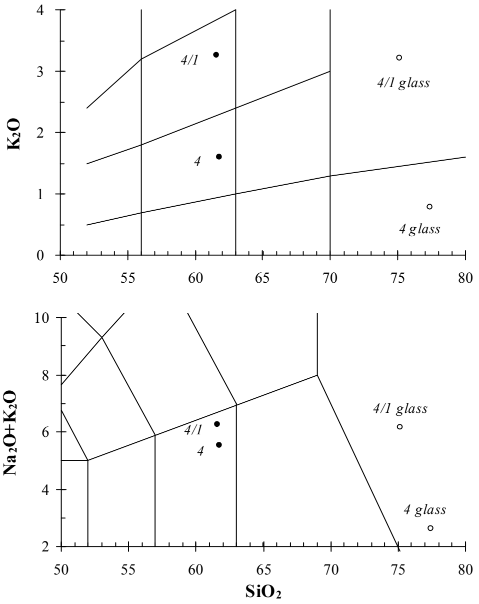

Fig. 2. K_2O (in the top) and Na_2O+K_2O (in the bottom) vs. SiO_2 diagrams with the points of studied Cs-bearing volcanics and their glassy groundmass (4/1-high K andesite and 4-hyaloandesite). Classification fields is according to Peccerillo and Taylor (1976) and Le Maitre (1989) respectively
Фиг. 2. K_2O (горе) и Na_2O+K_2O (долу) vs. SiO_2 диаграми с фигуративните точки на изследваните Cs-съдържащи вулканити и тяхната стъклена основна маса (4/1-високо-калиев андезит, 4-хиалоандезит). Класификационните полета са съответно според Peccerillo & Taylor (1976) и Le Maitre (1989)

The two volcanic rocks are characterized by elevated content of Cs (Table 1) which varies between 50 and 215 ppm (average 143 ppm) in the high-potassium andesite and between 42 and 345 (average 152 ppm) in the hyaloandesite (Marchev, 1979).

Microprobe analyses (Table 1) undoubtedly show that Cs is concentrated in the groundmass glass. The content of Cs is higher in the glass of high-potassium andesite, where the quantity of glass is smaller. In the last 10 out of 11 measured points the content of Cs is between 120 and 1990 ppm (an average of 760 ppm), but only 12 out of 19 analyses in the hyaloandesite glass show Cs content within the range of 200-1360 ppm (an average of 363 ppm).

Phenocryst phases also contain certain amounts of Cs (Table 2 and 3). In the high-potassium andesite, it was detected in the orthopyroxene and plagioclase. Some 7 out of 10 analyzed crystals of orthopyroxene show variations between 40 and 500 ppm. In contrast, all hyaloandesite phenocrysts (amphibole except) contain Cs (Table 2 and 3) with highest concentrations measured in orthopyroxenes where 12 out of 16 analyzed crystals contain Cs between 40 and 840 ppm. Some 4 out of 6 analyzed clinopyroxene crystals show Cs content from 120 to 670 ppm, which is similar to those in the clinopyroxenes (110-130 ppm) from the Cs-bearing Borovitsa absarokite (Yanev, 1994b). Some 4 out of 12 analyzed biotites have measurable concentration of Cs within the range of 40-610 ppm.

Based on the data obtained, the following average partition coefficients (K_d) between minerals and groundmass, were calculated in the hyaloandesites (Table 3): orthopyroxene – 0.99, plagioclase – 0.83, clinopyroxene – 0.74 and biotite – 0.25. For orthopyroxene in high-potassium andesite K_d is considerably lower (0.18). Liakhovich (1973) reported a little different order (orthopyroxene>biotite>plagioclase) for a vitrophiric andesite dyke from the Caucasus, containing 22.6 ppm Cs. This order of enrichment is unusual and most workers consider the biotite structure the most favorable to accommodate the large Cs ion (Tauson, 1961; Antipin et al., 1984; Villemant, 1985).

The established partition coefficients of the Borovitsa andesites are problematic because of the wide range of values measured in the crystals of the same rock.

Partition coefficients for Cs have rarely been reported in literature. The only known data come from high- to ultra-potassium rocks with lower content of Cs from Massif Central, France, Phlegrean Fields, Italy (Villemant, 1985, 1988) and Borovitsa area (Karadjov, Karadjova, 1998). These authors present data for the intermediate rocks, but their K_d is lowerthan our results. Partition coefficients for

Table 2. *Microprobe analyses of the plagioclase phenocrists in Cs-bearing andesites*

Таблица 2. *Микросондови анализи в Cs-съдържащите андезити*

Samples	4/1				4								
Points	81 rim	82 rim	83 rim	84	124 rim	125 core	126 rim	128 rim	129 core	130 core	53	29	40
SiO_2	55.47	58.69	58.79	55.96	58.22	58.33	55.94	57.77	55.63	52.16	52.86	58.48	52.86
TiO_2	0.00	0.04	0.04	0.00	0.00	0.00	0.00	0.13	0.02	0.03	0.15	0.00	0.04
Al_2O_3	26.69	25.31	24.77	26.41	24.82	24.97	26.37	25.64	26.61	28.97	27.86	25.60	28.39
FeO	0.42	0.51	0.55	0.46	0.45	0.40	0.58	0.26	0.41	0.34	0.53	0.48	0.46
MnO	0.01	0.06	0.08	0.00	0.01	0.02	0.00	0.04	0.00	0.05	0.00	0.03	0.00
MgO	0.06	0.05	0.06	0.03	0.03	0.04	0.14	0.03	0.03	0.05	0.04	0.04	0.03
CaO	9.48	7.63	7.47	9.42	7.88	7.72	9.30	7.89	9.16	12.53	10.96	8.70	11.65
Na_2O	5.08	6.28	5.81	5.50	5.57	6.15	5.08	5.85	5.46	3.95	4.61	5.99	4.60
K_2O	0.94	1.21	1.61	0.80	1.72	1.13	1.00	0.95	0.83	0.41	0.57	0.97	0.53
Total	98.15	99.78	99.13	98.58	98.68	98.89	98.51	98.55	98.16	98.52	97.57	100.28	98.56
Cs (ppm)	n. d.	n. d.	200	n. d.	n. d.	1310	1000	n. d.	n. d.	360	n. d.	n. d.	n. d.
Si	2.547	2.641	2.662	2.559	2.651	2.649	2.561	2.625	2.552	2.405	2.455	2.622	2.435
Ti	0.000	0.001	0.001	0.000	0.000	0.000	0.000	0.005	0.001	0.001	0.005	0.000	0.001
Al	1.444	1.342	1.321	1.423	1.332	1.337	1.423	1.373	1.439	1.575	1.525	1.353	1.541
Fe	0.016	0.019	0.021	0.017	0.017	0.015	0.022	0.010	0.016	0.013	0.021	0.018	0.018
Mn	0.000	0.002	0.003	0.000	0.000	0.001	0.000	0.001	0.000	0.002	0.000	0.001	0.000
Mg	0.004	0.003	0.004	0.002	0.002	0.002	0.009	0.002	0.002	0.003	0.003	0.003	0.002
Ca	0.466	0.368	0.362	0.462	0.384	0.376	0.456	0.384	0.450	0.619	0.545	0.418	0.575
Na	0.452	0.548	0.510	0.487	0.492	0.542	0.451	0.515	0.486	0.353	0.415	0.521	0.411
K	0.055	0.070	0.093	0.046	0.100	0.065	0.059	0.055	0.049	0.024	0.034	0.055	0.031
An	47.9	37.3	37.5	46.4	39.4	38.2	47.3	40.2	45.7	62.1	54.9	42.0	56.6
Ab	46.4	55.6	52.8	49.0	50.4	55.1	46.7	54.0	49.3	35.5	41.7	52.4	40.4
Or	5.7	7.1	9.6	4.7	10.2	6.6	6.1	5.7	4.9	2.4	3.4	5.6	3.0

n. d. - not detected

n. d. – под чувствителността на анализа

Table 3. *Average microprobe analyses of the mafic phenocrists in Cs-bearing andesites*
Таблица 3. *Микросондови анализи (ср. съдържания) на фемичните фенокристали в Cs-съдържащите андезити*

Minerals	Orthopyroxene		Clinopyroxene			Biotite		Amphibole
Samples	4/1	4	4/1		4	4/1	4	4
	n=10	n=16	n=1 (core)	n=2 (rim)	n=6	n=4	n=12	n=1
SiO_2	53.84	52.82	51.70	51.81	51.76	36.16	36.26	41.39
TiO_2	0.21	0.21	0.37	0.59	0.25	4.94	5.12	3.35
Al_2O_3	0.89	0.88	2.11	2.71	1.22	13.55	13.44	11.84
FeO	17.37	18.27	6.47	8.46	7.86	13.00	12.95	10.38
MnO	0.64	0.69	0.13	0.29	0.39	0.10	0.09	0.04
MgO	24.44	24.29	17.41	14.38	15.07	15.24	15.29	13.91
CaO	1.33	1.16	20.49	20.96	21.14	0.00	0.01	11.43
Na_2O	0.03	0.03	0.30	0.47	0.36	0.64	0.66	2.24
K_2O	0.02	0.02	0.01	0.00	0.00	8.69	8.64	1.30
Total	98.80	98.46	98.98	99.67	98.08	92.32	92.47	95.88
Cs (ppm)	140	360			270		90	
K_d^{Cs}	0.18	0.99			0.74		0.25	
Si	1.987	1.970	1.922	1.932	1.960	5.542	5.545	6.183
Ti	0.006	0.006	0.010	0.017	0.007	0.569	0.589	0.376
Al^{IV}	0.010	0.029	0.078	0.069	0.040	2.435	2.422	1.817
Al^{VI}	0.028	0.009	0.014	0.050	0.015	0.012	0.001	0.269
Fe^{3+}								0.155
Fe^{2+}								1.142
Total Fe^{2+}	0.537	0.570	0.201	0.264	0.249	1.667	1.657	
Mn	0.020	0.022	0.004	0.009	0.012	0.012	0.012	0.005
Mg	1.346	1.351	0.965	0.799	0.851	3.484	3.487	3.097
Ca	0.053	0.046	0.816	0.837	0.858	0.000	0.002	1.830
Na	0.002	0.002	0.022	0.034	0.026	0.190	0.195	0.646
K	0.001	0.001	0.000	0.000	0.000	1.700	1.685	0.248
Mg/(Mg+Fe)	71.5	70.3	82.7	75.2	77.4	67.7	67.8	70.5

K_d^{Cs} - Cs distribution coefficient phenocrist/glass; n - number of analyzed sample
K_d^{Cs} - Коефициент на разпределение на Cs фенокристал/стъкло n – брой на анализираните образци

clinopyroxene in latites from the Phlegrean Fields and Borovitsa are similar (0.02-0.28 and 0.14-0.25, respectively) and much higher than those from Massif Central (0.04-0.07). K_d for orthopyroxene was calculated only in the Borovitsa intermediate rocks (Karadjov, Karadjova, 1998), varying between 0.15 and 0.42. Higher K_d for the same mineral, close to our results, was calculated in vitrophire andesite with elevated content of Cs from the Caucasus (0.75 - Liakhovich, 1973). Only the partition coefficients for the biotite are higher than our K_d, increasing from the Phlegrean Fields (0.38 - Villemant, 1988), through Massif Central (0.5-1.39 – Villemant, 1985), to Borovitsa (1.55-3.43).

Discussion and conclusion

The explanation of the high contents of Cs in the andesites groundmass and in their phenocrystals is different. Their groundmass is similar to the high-Cs perlites being of glassy structure and rhyolitic composition. Cs in the high-Cs perlites is probably incorporated in the glassy structure because it could be extracted only after complete dissolution of the glasses and microprobe analyses cannot detect any Cs mineral (Shatkov, 1971; Yanev, Karadjova, 1976; Yanev, 1994a). Along with the ions of the other alkaline and alkaline-earth elements, Cs plays the role of a modifier, which compensates the negative charge of the Al-Si framework of the glass. The strongly deformed glassy structure contains "cavities" whose radii increase with increasing the Si/Al ratio. The "cavities" radii of the rhyolites reach up to 2.7-3.4 Å due to their very high Si/Al ratio (Chelishchev et al., 1974). Thus, the rhyolite glasses are most suitable to accommodate the large Cs ion. This explains the Cs enrichment in the groundmass glasses of the studied andesites of rhyolitic composition.

In the phenocrysts Cs concentrates to the highest degree in orthopyroxene. According to Stavrov (1978), the incorporation of Cs in some mafic minerals such as olivine and, particularly pyroxenes, is facilitated by the variable octahedral positions of Mg and Fe^{2+}. This allows alkaline elements (A), including those with the largest ions, to replace Mg and Fe^{2+} by heterovalent isomorphism according to the following patterns: $Mg+Fe^{2+} \rightarrow A+Fe^{3+}$, $2Mg^{2+} \rightarrow A+Fe^{3+}$ or $2Fe^{2+} \rightarrow A+Fe^{3+}$. The appearance of Fe^{3+} ion causes "withdrawal" of 2p oxygen electrons from the neighboring octahedral positions towards Fe^{3+}, which allows accommodation of ions much larger than those of Mg and Fe^{2+}.

The major results of this study are as follows:

(1) Cs in the Cs-bearing intermediate rocks is concentrated in their glassy groundmass of rhyolite composition;

(2) Some phenocrysts have Cs contents, measurable with microprobe, of the highest concentrations surprisingly found in orthopyroxene.

However, a high resolution study, including LAICP/MS, may produce better results for the content of Cs in phenocrysts that can facilitate understanding the influence of various parameters controlling partitioning between phenocrysts and glass in these Cs-bearing rocks.

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