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Chemical composition and geochemical characteristics of the Svidnya magmatic potassic-alkaline association, Western Stara Planina Mountain

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Abstract. The potassic-alkaline rocks of the Svidnya magmatic association (dated c.a. 320-340 Ma) outcrop as small hypabissal bodies, apophyses and dykes emplaced into argillites and quartzites of Ordovician. The main intrusive bodies consist of early potassic clinopyroxene-biotite shonkinites (phase I), which are cut by small dykes of potassic-alkaline biotite-amphibole syenite porphyries (phase II), and followed by intrusive bodies and dykes of potassic-alkaline aegirine-augite quartz syenites (phase III), and late dykes of potassicalkaline amphibole-aegirine syenite porphyries (phase IV). Besides, shlieren and segregations of biotite pyroxenites and glimmerites were established, with gradual transitions to shonkinites. Some additional rock types were also found: potassic biotite-amphibole shonkinite, melanocratic potassic-alkaline amphibole syenite and potassic-alkaline amphibole quartz syenite and potassic clinopyroxene-amphibole syenite. Late carbonate veins (carbonatites) cut the rocks.

In general, the rocks are characterized by high content of alkalies and especially of K, high K/Na ratio, enrichment of Ba and Sr, depletion of Al_2O_3 , etc. Some trends during the magma evolution may be noticed: decrease of MgO, CaO, Cr₂O₃, NiO content, and ratio K/Na, increase of the agpaitic coefficient Ka, of the content of Th, U, Zr and Mg# at the last stages. Rocks are enriched in REE (Σ REE from 187 up to 811 ppm), with the light REE prevailing over the heavy REE, with a low negative anomaly and similar REE pictures for the various shonkinites and syenites. The geochemical data confirm the common genesis and argue the homodromous formation of the Svidnya magmatic rocks. On the other hand, the variability in some chemical and mineral characteristics reflects the irregularity of processes of magma differentiation and crystallization even at a short distance. Geochemically (but not mineralogically), the Svidnya rocks show considerable similarity to the lamproitic series of the Aldan Shield and especially to their intrusive rock.

Key words: potassic-alkaline rocks, shonkinite, agpaitic syenite, biotite pyroxenite, Svidnya magmatic association

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Владыкин Н. В., Л. А. Грозданов, И. К. Бонев. 2001. Химичен състав и геохимични характеристики на Свидненската магматична калиево-алкална асоциация, Западна Стара планина. - *Геохим., минерал. и петрол.*, **38**, 3-22.

Резюме. Калиево-алкалните скали от Свидненската магматична асоциация, чиято възраст се определя на 320-340 Ма, се разкриват като малки хипоабисални тела, апофизи и дайки, вместени в ордовикски аргилити и кварцити. Приема се, че главните интрузивни тела са съставени от ранни калиеви клинопироксен-биотитови шонкинити (I фаза), пресечени от малки дайки на К-алкални биотитамфиболови сиенит-порфири (II фаза), следвани от интрузивни тела и дайки на К-алкални кварцсиенити (III фаза) и късни дайки от К-алкални амфибол-егирин сиенит-порфири (IV фаза).

Допълнително бяха установени шлири и сегрегации от биотитови пироксенити и глимерити, постепенно прехождащи в шонкинити, както и калиеви биотит-амфиболови шонкинити, меланократни К-алкални амфиболови и К-алкални амфиболови кварц-сиенити и калиеви килнопироксенамфиболови сиенити. Скалите се пресичат от късни карбонатни (карбонатитови) жили.

Най-общо, скалите се характеризират с високо съдържание на алкалии и особено на K, обогатени са на Ba и Sr, обеднени на Al_2O_3 . Забелязват се някои тенденции в хода на магмената еволюция, като намаляване съдържанието на MgO, CaO, Cr₂O₃ и NiO, на K/Na отношение, заедно с увеличаване на агпаитовия коефциент Ka, на съдържанието на Th, U, Zr и на Mg# в късните фази. Скалите са набогатени с редкоземни елементи (ΣREE от 187 до 811 ppm), с преобладание на леките над тежките елементи, при неголяма отрицателна Eu аномалия и твърде сходни криви на разпределение при различните разновидности шонкинити и сиенити. Геохимичните данни потвърждават генетичната общност и аргументират хомодромно формиране на скалите от Свидненската магматична асоциацията. Вариациите в някои химични и минерални характеристики, от друга страна, отразяват някои неравномерности в процесите на магмената диференциация и кристализация, дори на кратки разстояния. Геохимично (но не и минераложки), Свидненските скали показват значително сходство със скалите от лампроитовата серия на Алданския щит, и по специално с нейните интрузивни представители.

Ключови думи: калиево-алкални скали, шонкинити, агпаитови сиенити, биотитови пироксенити, Свидненска магматична асоциация

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Introduction

The specific association of Svidnya magmatic potassic-alkaline rocks occurs in the vicinity of the Svidnya Village, about 30 km N of Sofia, in the Western Stara Planina Mountain. These rocks form hypabyssal bodies, apophyses and dykes (Fig. 1) intruded within the Ordovician argillites and quartzites, and occupying a total area of about 2,5 km² (42°55'-42°57' N, 23°16'-23°18'E).

The Svidnya potassic-alkaline rocks are known since a long time and have been object of a considerable number of publications (Bončev, 1908; Andreev, 1910; Dimitrov, 1937, 1939, 1946, 1955, 1958; Mintscheva-Stefanova, 1951; Nikiforov, 1956; Dragov, 1962; Grozdanov, 1963, 1965, 1966, 1969, 1970a, 1970b, 1978, 1979, 1999; Poulieff, 1964; Arnaudov, Petrusenko, 1965; Aleksiev, 1965, 1966; Aleksiev et al., 1966; Stefanova, 1966a,b, 1967, 1976; Lilov et al., 1968; Voutov, 1973; Stefanova, Boyadjieva, 1974, 1975; Stefanova et al., 1974; Grozdanov et al., 1980; Amov et al., 1981; Palshin et al., 1989; Stoykov, Bojkov, 1991; Hadjiev, Ivanov, 1996). Diverse information is provided in these articles on the petrology of rocks, their mineral and chemical composition, classification position, crystallization and differentiation features, postmagmatic alterations, aplitepegmatite mineralizations, age, geodynamic setting and usage as a complex mineral raw material. Nevertheless, a number of questions remain open. New studies, based on modern methods are needed to understand this peculiar magmatic association with so far not known full analogue.

In this work, new chemical data are presented with the aim to extend our knowledge on the geochemistry of the magmatic rocks from the Svidnya association, both for major and trace elements, and on this basis to derive some trends in their differentiation. Some new rock types for the area were also described. Confirming that the composition of the Svidnya magmatic rocks is close to that of the lamproites, we present some comparisons with the well characterized potassic-alkaline intrusive rocks of the lamproitic magmatic complex of the Aldan Shield (Vladykin, 1997a,b 2000).



Fig. 1. Geological scetch of the vicinity of the Svidnya Village and its quarters, with outcrops of various types of potassic-alkaline intrusive and dyke rocks (modified from Dimitrov, 1937) Фиг. 1. Геоложка скица на района на с. Свидня с нейните махали, показваща разкритията на

различните типове калиево-алкални интрузивни и дайкови скали (модифицирана, по Dimitrov, 1937)

Petrological review

The petrographic description of the main magmatic rocks of the Svidnya association have been given firstly by Andreev (1910) and Dimitrov (1937), and of some additional rock types, by Grozdanov (1965, 1999) and Voutov (1973). Dimitrov (1937) distinguished three well individualized groups of successively intruded rocks. Phase I includes potassic shonkinites, represented by aegirine-augite-biotite shonkinites (with augite grading to aegyrinaugite towards the periphery of the crystals), augite-katophorite shonkinites (with katophorite shonkinites (with shonkinites (w

nites with biotite, all related by gradual transitions. Quartz-bearing amphibole-("uralite")biotite monzonites (iogoites), locally with corroded andesine, were also referred to this phase I. Based on the chemical rock composition, the basic shonkinite varieties were assumed to be close to jumilites and orendites but without leucite. Phase II includes potassicalkaline aegirine-amphibole quartz syenites, showing two differentiation trends. The first trend covers mafite-rich varieties denoted as facies of tinguaite schlieren, and the second, of very leucocratic rocks. A porphyric (orthophyric) facies of mesocratic character, typical of the peripheral parts of larger bodies and in particular of veins, and a specific tinguaite facies, were also distinguished. Phase III comprises only dyke rocks denoted as potassicalkaline quartz-tinguaite porphyries (grorudite porphyries) or aegirine-amphibole porphyries. Later, Grozdanov (1965) established thin veins of potassic-alkaline biotite-hornblende porphyries that cut the pyroxene-biotite shonkinites and form xenoliths in the potassic-alkaline aegirine-amphibole quartz syenites. For this reason they were described as phase II, while phase II and III of Dimitrov (1937) were referred to as phase III and IV, respectively. A comparative overview of the now known magmatic rock types is given in Table 1.

Voutov (1973) described specific biotiteamphibole minettes, melanocratic solvsbergites and solvsbergite porphyries, assumed to be analogues of the quartztinguatite porphyrites and solvsbergite, tending to tinguaite. Recently, Grozdanov (1999) described another vein rock, alkaline aegirine-magnesio-arfvedsonite syenite porphyry of the K-Na series, which intersects pyroxene-biotite shonkinites.

Dragov (1962) compared the potassic rocks from different localities in the Stara Planina Mt. and Kraishte area, according to their chemical composition. The shonkinites from Svidnya association he referred to the slightly alkaline potassic-magmatic rocks, and the potassic-alkaline quartz syenites with their tinguaite facies and the potassic-alkaline quartz tinguaite porphyries to the group of potassicrocks with high alkalinity. He marked the increased role of Na during the magma differentiation.

Dimitrov (1937), analyzing the formation of the Svidnya shonkinites mentioned a distinctly expressed lamproite tendency in magma differentiation. Stefanova (1966a,b), on the basis of published chemical analyses and own data, developed the idea for affiliation of the Svidnya magmatic rocks to lamproites, as heteromorphic to wyomingites, including not only the more basic rocks of phase I but also all potassic-alkaline rocks in the area. For the three phases of Dimitrov she introduced new

leucolamproites lamproites. and terms: lamproite porphyrites. The absence of leucite in Svidnya rocks (the main mineral in wyomingites) was explained by their hypoabissal setting, favouring crystallization of biotite and amphibole which contain less SiO₂ than orthoclase, thus compensating the deficiency of SiO₂ (Aleksiev et al., 1966; Stefanova, 1967, 1976). Stefanova et al. (1974) reached the conclusion for considerable in range postmagmatic alterations in the Svidnya magmatites. The end stage of these alterations was described as aegirine autometasomatism. The rocks of phase I are most intensively affected by these alterations. Stefanova (1976; Stefanova, Boyadjieva, 1975; Stefanova et al. 1974), based on the assumption for two intrusive phases and two subsequent groups of vein rocks, presented a detailed concept on development of these magmatism. In fact, again a four phase intrusive process is advocated. A number of new terms were also introduced: own magmatic biotite lamproites, biotite-amphibole lamproites, svidneite-, svidneite-aegirine- and aegirine lamproites, biotiteactinolite lamproites, katophorite lamproites and melanocratic autometasomatites.

Foley et al. (1987, Table I), on the basis of published by Stefanova (1966a) chemical analyses, determined these magmatites as ultrapotassic rocks (K₂O>3 wt.%, MgO>3 wt.% and K₂O/Na₂O>2) and referred them to group IV, which is transitional between the three main groups: group I - lamproites, group II - kamafugites and group III - rocks of the orogenic areas. Thus, they disputed the affiliation of the Svidnva rocks to lamproites. It should be also taken into consideration that lamproites, as typically effusive rocks, have a specific mineral composition and textures, contain specific accessory minerals like priderite and vadeite, but no aegirine, etc. (Bogatikov et al., 1985; Foley et al., 1987; Mitchell, 1988; Le Maittre, 1989; Wilson, 1989; Panina, Vladykin, 1994; Műller, Groves, 1995; Vladykin, 1997a,b).

I-I	Main intrusive phases: V, after Dimitrov, 1937, and Grozdanov, 1965;): after Stefanova, 1966	Petrographic type and facies	Relationships	Mineral composition	Mineral symbols
I	Potassic shonkinites (lamproites) Potassic-alkaline	 Bt pyroxenites and glimmerites (this work) Cpx-Bt shonkinites Bt-Amp syenite porphyries 	 schlieren and segre- gations in shonkinites main intrusive rocks dykes cutting I, and 	Bt 80-90% Cpx, Kfs, Ap Kfs, Cpx, Bt Kfs, Bt, Amp	<u>magmatic minerals:</u> K-feldspar (Kfs) biotite (Bt)
	syenite porphyries		xenoliths in III		augite (Aug)
III	Potassic-alkaline quartz syenites (leycolamproites)	-Ae-Amp quartz syenites and quartz syenite porphyries - tinguaites - leucocratic ortophyres	 inrtusive rocks and dykes cutting I schlieren-like facies peripheral facies 	Kfs, Amp, Ae, Q	amphibole (Amp) aegirine (Ae) Mg-arfvedsonite (Arf) clinopyroxene (Cpx)
IV	Potassis-alkaline "quartz-tinguaite" porphyries (lamproite porphyries)	 Amp-Ae syenite porphyries (this work) solvsbergite (Vutov, 1973) 	- dykes cutting I and III	Kfs, Ae, Amp, Q	quartz (Q) apatite (Ap) magnetite (Mgt) calcite (Ca)
-	Other single rock samples, in not exactly determined relations to the main phases	- alkaline Ae-Arf syenite porphyries (Grozdanov, 1999) - Bt-Amp minette - (Vutov, 1973) - Bt-Amp shonkinite (this work) - Amp-Q syenite - Amp syenite - Cpx-Bt syenite - carbonatites "	- dykes cutting I not fully defined	 Са, Ар	not detected: leucite (Leu) nepheline (Ne) olivine (Ol)* (pseudo- morphed by Bt+Amp)

Table 1. Potassic-alkaline magmatic rocks of the Svidnya association (according to published data) Таблица 1. Калиевоалкални маматични скали от Свидненската асоциация (по литературни данни) Geochemical peculiarities of the Svidnya magmatic association were studied by Dimitrov (1937), Nikiforov (1956), Aleksiev (1965, 1966, etc.) Stefanova (1966a,b, etc.), Stoykov, Bojkov (1991) and other authors. Between the other characteristics it was established that the rocks have enhanced concentrations of Ba, Sr, Zr, Th, U, REE, etc.

Age

Andreev (1910) and Dimitrov (1937) have shown that the argillites and quartzites (considered as Silurian) embedding the intrusive bodies of the Svidnya association, have been undergone to rather intensive contact metamorphism. A pre-Upper Carboniferous (Sudetian) age of the magmatism was assumed. The lack of intrusive clasts in the nearby exposed Upper Carboniferous sediments was ascribed to the absence of relevant rock exposures at that time (Dimitrov, 1937).

Recently, the host sediments were assigned to the Ordovician Grohoten Formation (Spasov, 1960; Yanev, 1995). New biostratigraphical data precise the age of this formation as Oretanian, Dobtrotivian, Berunian and Ashgilian (Gutierrez-Marco et al., 2002). The Ordovician in the studied area is considered as a part of the peri-Gondwanian Balkan terrane, disposed at a latitude of 40° South (Yanev, 2000). Rocks, comparable to those of Svidnya association, were found in the conglomerates of the Birimirtsi Formation of molasse type Lower the Permian "Rhotliegend" (Zhukov et al., 1976; Yanev, 1982).

The absolute age datings vary in a wide range. Biotite K-Ar data from pyroxene-biotite shonkinite (Lilov et al., 1968) yield 340 Ma, thus suggesting that the Svidnya magmatites were formed at the boundary between the Devonian and the Carboniferous or close to that interval. Isotope Pb composition of Kfeldspars and accessory galena (Stefanova et al., 1974) indicate 330±20 Ma. Amov et al. (1981), based on U-Pb methods, report 315±20 Ma (²⁰⁸Pb/²³⁵U) and 321±18 Ma (²⁰⁷Pb/²³⁸U) for apatite, 435, 425, and 390 Ma from uranogenic Pb of K-feldspar, and 330, 320, and 280 Ma from thorogenic Pb of K-feldspar. Palshin et al. (1989) through K-Ar dating of alkaline quartz syenites from three points yield much younger, Mesozoic ages, in the interval 120-130 to 200 Ma. However, such large discrepancy in the time of formation of these closely spatially, petrologically and geochemically related rocks seems unrealistic.

Materials and methods

25 representative samples were selected for this study with the aim to characterize the different rock types and variet)es and the evolution of the magmatic process (Table 2). It must be pointed out that the poor exposures, intensive tectonic impact and weathering impede a detailed sampling of the whole Svidnya area.

The studied samples cover mainly the western part of this area where the magmatic rocks are relatively better exposed. Most samples were collected from rock outcrops but some are from singular gravels of more specific rock varieties. Samples assumed to be influenced by the early autometasomatic katophorite alterations over-printed on early shonkinites (e.g. augite-biotite-katophorite shonkinites), and the later, mainly aegirine and amphibole alterations on syenites and dykes (Stefanova, 1966a,b, 1976, etc.) are not discussed here.

For denoting the main rock types of the Svidnya intrusive association, following Dimitrov (1937), we use the adequate terms *shonkinite* and *syenite*, specifying their mineral composition. The dyke rocks are denoted as respective *porphyries*. We consider the nomenclature of the effusive lamproites not directly applicable to intrusive rocks, even when they are chemically very similar. Such approach is commonly accepted (e.g. Shadenkov et al., 1989).

Five are the main points of rock sampling (A-E) and they are marked on the map of Fig. 1, as follows: A - the left bank of Svidnya River below Pessoko Quarter; B - an outcrop

on the right bank of Svidnya River, along the motor road to Chibaovtsi Village; C northwestern slope of the Lilyako height; D nearby Padej Quarter; E - along the slope, west of Padej Quarter. Some new for the area rock varieties were established, including *biotite pyroxenite* with transitions to *glimmerite*, *biotite-amphibole shonkinite*, *clinopyroxenebiotite syenite*, *amphibole syenite*, and *carbonatites*.

All rock samples were analyzed for the main components by wet chemical silicate analyses. The content of rare and rare-earth elements was determined by using of ICP MS. The analyses were performed in the laboratories of the Institute of Geochemistry of the Siberian Branch of the Russian Academy of Sciences in Irkutsk by the analysts N. M. Behtereva and A. Ju. Mitrofanova, respectively. The detailed studies of rockforming minerals, which are in progress, are not reported here.

Mineral and chemical composition, and petrochemical characteristic of rocks

Biotite pyroxenites and *glimmerites* are the earlist rock types, first documented now for the Svidnya magmatic association. They occur as shlieren and local segregations into shonkinites, reaching from 2-4 m up to 10-50 m in size. Established were in two small intrusive shonkinite bodies outcropped along the Svidnya River (Fig. 1). The gradual

Таблица 2. Изследвани скални образци

No	Samp	Petrographic type	General characteristic and mineral	Phase	Sample
	le		composition, ~%		place
1	29	glimmerite	melanocratic, medium-grained, Bt ≥90		Α
2	55	Bt pyroxenite	melanocratic, fine- to medium-grained		В
3	56	Bt pyroxenite	Bt 80, Cpx 5, Kfs 10, Ap 5		В
4	16	Cpx-Bt shonkinite			Α
5	18	Cpx-Bt shonkinite	melanocratic,	Ι	A
6	26	Cpx-Bt shonkinite	fine- to medium-grained,		Α
7	28	Cpx-Bt shonkinite	Kfs 50-60, Bt 15-25,		Α
8	50	Cpx-Bt shonkinite	Cpx 15-25, Amp 1-5		В
9	53	Cpx-Bt shonkinite			В
10	17	Bt-Amp syenite porphyry	mesocratic, porphyres of Kfs 30, Bt 10, Cpx 5	II	Α
11	38	Ae-Amp syenite	melanocratic		С
12	42	Ae-Amp-Q syenite	meso- to leucocratic, pale yellow to rose-		D
13	45	Ae-Amp-Q syenite	coloured, medium-grained	III	D
14	47	Ae-Amp-Q syenite	Kfs 50-80, Amp 15-30,		D
15	48	Ae-Amp-Q syenite	Ae 5-15, Q 5-15		D
16	21	Amp-Ae syenite porphyry	grey-greenish,		Α
17	22	Amp-Ae syenite porphyry	medium-grained,		Α
18	23	Amp-Ae syenite porphyry	porphyres: Kfs 5-15, Ae 5-10, Amp 5-10,	IV	Α
19	52	Amp-Ae syenite porphyry	groundmass: Kfs 30, Ae 15, Amp 10, Q 5		В
20	20	Bt-Amp shonkinite	melanocr., medium-gr., Kfs 55, Amp 30, Bt 15		Α
21	37	Amp syenite	melanocr., grey, fine-gr., Kfs 50, Amp 50	single	E
22	36	Amp syenite	leucocr., fine-gr., Kfs 70, Amp 30	rock	Е
23	40	Amp syenite	melanocr., medium-gr., Kfs 70, Amp 30	samp-	Е
24	25	Amp-Q syenite	grey, medium-porphyric, Kfs 60, Amp 25, Q15	les	Α
25	35	Cpx-Bt syenite	rose, medium-gr., Kfs 80, Bt 10, Cpx 5, Mgt 5		Е

Sampling places: A - Pessoko; B - the right bank of Svidnya River; C - Padej; D - northern slope of the Lilyako height; and E - west of Padej

Phase		Ia				II	III				
Rock	Glimme-	Bt pyro	oxenite			Bt-Amp syenite Ae-Amp					
	rite				-						Q syenite
No	29	55	56	26	50	53	18	28	16	17	38
SiO ₂	36.12	40.55	44.41	50.32	50.45	52.24	52.66	52.74	53.64	56.76	56.45
TiO ₂	2.91	2.03	1.99	1.45	1.56	0.96	1.16	1.36	1.32	1.09	1.57
Al_2O_3	13.08	13.16	11.24	12.65	9.63	11.46	11.68	12.73	12.42	11.09	6.86
Fe ₂ O ₃	6.58	2.67	4.76	5.93	2.24	1.34	1.04	0.37	1.56	4.43	9.93
FeO	9.57	7.96	5.90	2.23	5.10	3.84	4.92	7.24	5.99	3.13	2.95
MnO	0.18	0.15	0.19	0.30	0.14	0.12	0.16	0.22	0.20	0.21	0.20
MgO	10.10	10.50	10.80	4.00	7.90	5.90	6.50	6.00	5.80	4.20	6.20
CaO	5.90	6.60	6.20	6.50	6.80	5.70	5.70	5.10	5.20	3.70	2.90
BaO	0.51	0.50	0.54	0.39	0.50	0.40	0.45	0.39	0.34	0.62	0.25
SrO	0.04	0.06	0.07	0.07	0.12	0.12	0.10	0.08	0.08	0.12	0.09
K_2O	6.62	5.85	5.49	6.46	7.35	8.30	8.25	7.67	7.80	9.00	5.65
Na ₂ O	0.38	1.02	0.75	1.62	1.36	1.52	1.37	1.87	1.78	2.59	5.29
P_2O_5	4.15	3.89	2.72	1.44	1.86	1.41	1.56	1.36	1.36	1.00	0.43
H_2O	3.34	4.34	4.51	3.23	3.27	4.43	2.10	1.57	1.53	1.48	1.23
F	0.45	0.50	0.35	0.16	0.21	0.16	0.19	0.19	0.21	0.13	0.14
CO_2	0.19	0.31	0.33	3.39	1.26	2.05	1.12	0.81	0.77	0.41	0.04
Total	100.12	100.09	100.25	100.14	99.75	99.95	98.96	99.7	100	99.96	100.18
Cr ₂ O ₃	946	555	1007	467	651	1068	557	566	540	306	338
NiO	232	109	188	106	129	162	110	118	113	72	95
Li ₂ O	442	262	179	167	92	69	50	133	100	35	54
Rb ₂ O	319	399	379	216	453	399	402	357	415	362	171
Cs ₂ O	17	13	14	11	19	19	16	25	24	9	4
Ka	0.596	0.609	0.638	0.763	1.058	1.002	0.957	0.894	0.915	1.262	2.159
Mg#	51.54	63.20	63.21	44.39	64.90	66.36	61.69	58.20	57.14	47.93	44.00
K/Na	11.67	3.88	4.83	2.65	3.55	3.52	4.00	2.70	2.86	2.29	0.71

 Table 3. Chemical composition of rocks from the Svidnya area

 Таблица 3. Химичен състав на магматични скали от района на Свидня

Phase		II	Ι		IV				Single rock samples					
Rock	Ae-Amp quartz syenite			Amp-Ae syenite porphyry				Bt-Amp shonki- nite	Cpx-Bt syenite			;	Amp-Q syenite	
No	42	48	45	47	21	22	52	23	20	35	37	40	36	25
SiO ₂	58.64	59.69	62.11	65.46	58.31	58.87	59.57	62.44	52.97	54.33	59.67	60.85	62.34	67.48
TiO ₂	0.98	1.20	0.62	1.36	0.96	1.05	1.72	1.08	1.17	1.59	1.34	1.29	0.91	1.83
Al_2O_3	9.91	10.69	12.45	12.06	11.63	10.67	9.20	10.40	10.23	13.16	9.66	10.12	12.24	8.62
Fe_2O_3	3.03	6.63	5.82	4.72	4.33	5.12	7.72	5.12	2.44	7.36	5.52	9.22	5.22	6.32
FeO	2.77	2.05	0.62	1.34	2.59	1.52	1.79	1.34	5.10	1.70	1.70	1.16	1.16	1.07
MnO	0.09	0.16	0.09	0.24	0.13	0.15	0.27	0.15	0.16	0.04	0.16	0.11	0.12	0.09
MgO	5.20	3.10	1.90	0.90	2.40	3.20	1.90	2.30	6.20	3.60	3.60	2.50	1.60	0.70
CaO	3.20	0.90	0.70	0.04	1.80	2.30	2.00	1.30	5.50	2.20	2.40	0.80	1.00	0.60
BaO	0.57	0.26	0.36	0.24	0.43	0.56	0.30	0.34	0.41	0.38	0.62	0.28	0.33	0.53
SrO	0.10	0.06	0.08	0.01	0.12	0.15	0.12	0.17	0.10	0.09	0.18	0.04	0.12	0.02
K_2O	10.05	9.30	11.15	10.75	9.60	9.70	7.30	8.55	7.23	10.20	8.50	8.60	9.65	7.38
Na ₂ O	1.77	3.67	1.77	0.23	3.20	3.31	3.49	3.58	1.78	0.24	3.67	3.57	3.58	3.58
P_2O_5	0.93	0.27	0.47	0.06	0.77	0.80	0.58	0.51	1.45	1.55	0.95	0.07	0.34	0.09
H_2O	2.02	1.48	1.47	2.67	3.35	1.62	2.91	2.46	3.00	2.76	1.51	0.57	0.90	1.26
F	0.16	0.10	0.10	0.02	0.09	0.14	0.07	0.10	0.20	0.14	0.16	0.05	0.07	0.02
CO_2	0.10	0.16	0.08	0.04	0.23	0.77	1.03	0.14	1.73	0.42	0.23	0.24	0.31	0.16
Total	99.52	99.72	99.79	100.14	99.94	99.93	99.97	99.98	99.67	99.76	99.87	99.47	99.89	99.75
Cr_2O_3	350	111	146	93	140	216	166	184	473	478	201	134	99	73
NiO	68	22	42	36	30	61	30	76	102	156	67	109	17	7
Li ₂ O	12	38	27	42	38	57	66	62	81	66	54	23	27	13
Rb ₂ O	407	467	479	453	366	408	419	382	366	367	333	407	333	329
Cs ₂ O	15	9	9	11	11	10	12	11	29	6	7	7	11	11
Ka	1.391	1.506	1.203	0.996	1.346	1.494	1.482	1.456	1.051	0.869	1.577	1.500	1.334	1.609
Mg#	60.00	36.84	31.97	19.30	54.55	43.89	24.48	36.54	58.56	39.04	44.72	27.93	28.99	12.98
K/Na	3.69	1.68	4.07	28.50	1.96	1.94	1.38	1.55	2.66	27.00	1.53	1.57	1.76	1.34

Table 3. *Continued* Таблица 3. *Продължение*

transitions to shonkinites suggest their formation in an process of early stratification of the initial potassium-alkaline ultrabasic magma.

The *biotite pyroxenites* are melanocratic medium-grained rocks, composed of biotite (\sim 50-70%), clinopyroxene (\sim 10-40%), and rare K-feldspar (1-5%). Indicative of them is the high amount of apatite, 3 to 7%, (compare Stefanova, Boyadjieva 1975). Locally, the biotite pyroxenites are transitional also to extremely biotite-rich rocks - *glimmerites* (or biotitites). They are made up of more than 90% biotite with only minor (up to 5%) K-feldspar and apatite.

The chemical analyses of biotite pyroxenites are shown in Table 3. Characteristic is the low content of SiO₂ (36-44 wt%) and Na₂O (0.38-1.02 wt.%), and the high content of TiO₂ (2-3 wt.%), MgO (10-11 wt.%) and P_20_5 (3-4 wt.%). Very high is also the sum $Fe_2O_3 + FeO$ (15 wt.%). The new data clearly exceed the limiting values known for the Svidnya magmatic rocks. The so far known minimum value of SiO2 was 46.38 wt.% (Stefanova, 1966 a,b). Lower were the known values (in wt.%) also of TiO₂<1.65, MgO<9, P2O5<2, Fe2O3 + FeO <11. The agpaitic coefficient, Ka = (K + Na)/Al of the biotite pyroxenites is especially low, 0.38, at a high K/Na ratio.

The shonkinites of the phase I of the Svidnya association occur in several small intrusive bodies (Fig. 1), as well as in veins cutting the embedding metamorphic rocks. In different degree they are affected by a later postmagmatic alteration with a partial replacemant of the clinopyroxenes by amphibole, and local formation of coarsegrained biotite. In the slightly alterated aegirine-augite-biotite shonkinites (Dimitrov, 1937), aegirine-augite is in fact a minor component in comparison to the main augite, that is why we will denote them as clinopyroxene-biotite shonkinites. The augitebiotite-katophorite and augite katophorite shonkinites, as affected by considerable autometasomatic alterations (Stefanova, 1976),

are not discussed here.

The *clinopyroxene-biotite shonkinites* are melanocratic, medium-grained rocks, composed of K-feldspar (50-60%), biotite (15-30%), clinopyroxene (10-20%), amphibole (1-5%) and apatite (1-3%). Occasionaly they include rounded biotite-amphibole aggregates, probable pseudomorphs after early olivine crystals. Similar formations are known and studied in details from the potassic-alkaline rocks of Aldan (Vladykin, 1997a,b, 2000), and from other regions as well (Foley et al., 1987). In the gruss of these rocks increased content of gold was also established.



Fig. 2. Correlation diagramms between some main chemical components for rocks of the Svidnya association: biotite pyroxenites and glimmerites (asterisks), shonkinites (squares) and syenites (circles), in wt.%

Фиг. 2. Корелационни диаграми за някои главни химични елементи в скалите от Свидненската асоциация: биотитови пироксенити и глимерити (звезди), шонкинити (квадратчета) и сиенити (кръгчета), в тегл. %



Fig. 3. Correlation diagrams between some main chemical components for lamproitic rocks of the Aldan Shield, in wt.%

Фиг. 3. Корелационни диаграми за някои главни химични елементи в лампроитовите скали от Алданския щит

According to their chemical composition (Table 3), the described here shonkinites can be clearly related to the ultrapotassic rocks (Foley et al., 1987). They show similarity with the shonkinites of the Aldan Shield (Vladykin, 1997a,b), but have some lower content of Al_2O_3 and CaO, and higher of BaO, K_2O , and K/Na ratio. It is important to mention that the shonkinites described here have no leucite, a common component for the volcanic rocks of such composition.

The syenites form small vein bodies which cut shonkinites, as well as larger stocklike bodies (Fig. 1), building elevated forms of the relief. They have diverse mineral composition. Some dykes are composed of melanocratic syenite porhyries with porphyric K-feldspar, biotite and pyroxene and finegrained groundmass of amphibole-feldspar composition. Other dyke syenites are composed of K-feldspar, alkali amphibole (5-30%) and alkali pyroxene (5-20%). Chemical analyses of syenites are presented in Table 3. Characteristic are considerable variations in SiO₂ composition (54-67 wt.%), MgO (from 1.9 up to 7.9 wt.%), low contents of Al_2O_3 , CaO, a high agpaitic coefficient, increased K₂O, TiO₂, BaO, SrO, and P₂O₅. Characteristic for these highly agpaitic syenite rocks is the presence of alkali pyroxenes and amphiboles and a high K/Na ratio which put them close to the potassic-alkaline series (with lamproites) of the Aldan Shield.

A peculiar *aegirine-hornblende quartz* syenite sample (No 38) originating from a more basic marginal facies, shows considerably lower Al_2O_3 content (6.86 wt.%) and the highest agaitic coefficient (2.16).

Between the samples of single gravels the following rocks were established.

• A *biotite-amphibole shonkinite* (sample No 20) found as a single piece of melanocratic, medium-grained potassic rock, in contrast to the usual shonkinites contains no clinopyroxene.

• *Potassic-alkaline amphibole syenite* (No 37), melanocratic, fine-grained, especially enriched in amphibole, differing from the known K-alkaline syenites by the absence of both biotite and aegirine.

• *Potassic-alkaline amphibole syenite* (No 36 and 40), grey, fine- to medium-grained rocks with low amphibole content, again without biotite or aegirine.

• *Potassic-alkaline amphibole quartz syenite* (No 25), grey, fine-grained, without biotite and aegirine.

• Potassic clinopyroxene-biotite syenite (No 35), medium-grained, with agpaitic coefficient 0.87. In relation to the femic minerals shows similarity with the clinopyroxene-biotite shonkinites, but with much higher quartz (respectively SiO₂) content. This rock has the lowest Mg# (Mg-number = 100Mg/(Mg+Fe)) = 12.98.

Though the direct relationships of these rocks to the main rock types are not observed, they are manifestation of the great heterogeneity and complexity of the processes of magma evolution.

In the region also some *carbonate rocks* were established, pertained to the latest mineral formations. They represent up to 2 m thick veins, cutting shonkinites. Composed are of calcite with some content of apatite (up to 5%) and mica (to 1%). Their preliminary study established considerable enrichment in Sr and Ba, suggesting that they are similar to *carbonatites* of the K-series, characterised by a low content of Nb, Zr and REE. Their more detailed study is in progress.

Correlation diagramms for some main chemical components of the rocks are shown in Figs. 2 and 4. In general, the main geochemical trends and correlations found by the previous authors were confirmed. Positive correlations, with some deviations, are seen between Al_2O_3 and SiO_2 , and between Al_2O_3 and K_2O (Fig. 2).

It is worth noting, that in the former discussions the role of magnesium is nearly not mentioned, though it is an important indicator for the magma genesis and differentiation processes. The diagramms on Fig. 2 show clear negative correlations MgO/K₂O and MgO/SiO₂.

A comparison of the correlation graphics of the Svidnya magmatic rocks and the intrusive rocks of the potassic-alkaline lamproitic rocks of the Aldan Shield (Figs. 3 and 4) indicates a close similarity between them, but with some specific differences. The content of Mg in Svidnya rocks is lower, and that of Fe is higher. Thus, on the triangle diagramms (Fig. 4) the biotite pyroxenite and olivine lamproites of Aldan extend much closer to the Mg-apex than the Svidnya rocks. In contrast, Al₂O₃ in the biotite pyroxenites of Svidnya is higher. According to the chemical composition, the shonkinites from Svidnya association are closer not to the lampoites themselves, but to the genetically related to them intrusive potassic-alkaline rocks of Aldan (Vladykin, 1989, 1997a,b). Taking in consideration the relations of Mg and Fe, a deeper generation of the potassic-alkaline magmas of Aldan can be assumed, as compared to the magmas in Svidnya.

Additional relations of Mg# with some characteristic chemical components of the Svidnya magmatic rocks are shown on Fig. 5. No clear correlation exists between FeO and MgO, when CaO and K/Na ratio are positively correlated with Mg#, decreasing to the late stages. The coefficient of agpaicity Ka = (K + Na)/Al covers a wide range (0.6 to 2.2), showing some trend to increase in the process of differentiation.

Composition of minerals

The main rock-forming minerals may be shortly characterised as follows. The micas are magnesium biotites refering to the flogopiteannite isomorphous series with rather high contents of TiO₂ (3-5 wt.%) and BaO (0.1-0.5 wt.%), with low Al₂O₃ and F (0.1-0.5 wt.%). The Al₂O₃ content decreases from the biotite pyroxenites (14-15 wt.%) to shonkinits (9-10 wt.%), in correlation with the increased agpaitic coefficient.

Amphiboles are often zoned and affected by postmagmatic alterations. According to their chemical composition they are related to



Fig. 4. Triangle diagramms for some main chemical components in rocks of the Svidnya magmatic association, in comparison to the lamproitic rocks of the Aldan Shield (area A), in wt.% Фиг. 4. Триъгълни диаграми за някои главни химични компоненти при скали от Свидненската магматична асоциация, в сравнение с лампроитовите скали от Алданския щит (поле A), в тегл. %

ekermanite in phase II, zoned richterite in phase III, zoned magnesio-arfvedsonite in phase IV, and to another homogenous magnesio-arfvedsonite, as was shown by Grozdanov (1963, 1969, 1999; Grozdanov et al., 1980). Feldspars are potassium-rich.

Behaviour of trace elements in the rocks

The content of trace elements in different rocks is shown in Table 3 and 4. With some exceptions, the new results confirm the published data giving more full and precise information. Interesting are the relatively high concen-trations of Ba (0.2-0.4 wt%) and Sr (280-1000 ppm) at a markedly predominance of Ba. The concentrations of Rb and Cs are lower, near the mean values for potassicalkaline rocks.

Some of the characteristic components of the rocks show more or less parallel decrease with the Mg# and in the course of the differentiation process. Such are Li₂O, BaO, SrO, Cs_2O , Cr_2O_3 and NiO_2 (Tables 3 and 4, Figs. 5 and 6).

Trends to increase the content to the later phases can be remarked for some other elements, like Zr and Hf, more distinct for Hf. These changes can be correlated with increase of SiO₂ content, and decrease of Mg# (Figs. 5 and 6), again. Nb and Ta and Nb/Ta are highly variable. The content of Nb records two weak maximums - at the beginning (sample No 29) and the end of the differentiation process (sample No 52). A late vein syenite porphyry (sample No 52), probably a final magma derivative, shows particularly high contents of Zr, Hf, Nb, Ta, Ti, Th and U. The ratio Th/U =5,48 in this rock, highest to the area, is closest to its average value of 5,2 for the Earth's crust according to Vinogradov (Table 1 in Smislov, 1974). Such enrichment at the end of the differentiation process was presumed (especially for Zr, Hf and Th) by Grozdanov (1965). Some other rare elements show irregular distribution during the magma differentiation.

	Phase	Ia	ı		Ib	II	Ι	II		IV		-
		glimme-	Bt	Ср	x-Bt	Bt-Amp	Ae-Am	p quartz				Amp
	Rock	ock rite pyroxe-		shonkinite		syenite	sye	nite	Amp-Ae syenite porphyry			syenite
			nite			porphyry			_			-
	N⁰	29	55	16	50	17	38	48	22	23	52	36
	Ba	3886	4012	2600	3622	4020	2032	2184	4142	2444	2839	2821
	Sr	278.53	368.24	588.85	851.85	817.81	843.11	397.77	1239.60	1430.40	951.08	1000.80
	Rb	401.84	368.58	363.55	366.94	313.33	214.39	411.27	366.89	367.48	362.77	356.02
	Zr	417.22	235.51	231.67	166.55	719.04	1747.70	818.12	627.02	491.00	3146.60	430.14
	Hf	8.23	5.88	7.17	6.43	21.83	53.11	25.03	15.54	14.11	83.82	12.20
	Nb	132.54	76.28	81.55	26.04	72.52	72.30	28.15	53.91	19.95	176.56	77.12
	Та	12.64	13.46	11.67	10.64	14.56	11.32	10.73	11.51	6.88	19.15	13.89
	Th	18.03	21.73	48.28	21.42	86.02	115.13	45.83	72.77	62.84	685.17	45.97
	U	11.30	7.80	10.63	4.60	19.08	23.46	8.56	21.32	13.55	125.06	18.28
_	Y	120.76	95.47	33.07	40.00	23.12	29.87	16.23	22.35	28.88	45.31	32.88
	La	130.88	131.28	88.53	93.11	63.49	73.07	41.21	87.22	141.30	105.06	105.31
	Ce	300.86	292.25	169.17	181.40	118.34	133.69	78.60	157.30	274.13	179.82	179.96
	Pr	43.73	40.80	20.74	23.51	14.61	15.94	9.55	19.05	33.00	20.90	20.09
	Nd	197.52	190.44	82.84	95.28	58.09	60.54	36.89	76.71	122.69	77.62	75.54
	Sm	48.50	39.79	16.39	19.86	12.22	12.91	7.97	15.51	25.45	16.26	14.33
	Eu	4.04	4.88	2.94	3.74	2.29	2.55	1.53	2.83	4.33	3.08	2.76
	Gd	30.73	23.90	9.20	11.68	6.59	6.66	4.12	7.51	11.64	9.08	8.27
	Tb	4.64	3.72	1.30	1.56	0.91	1.16	0.63	1.03	1.56	1.47	1.28
	Dy	23.99	17.49	6.10	8.09	4.51	5.36	3.15	4.35	6.81	7.14	6.19
	Но	4.78	3.90	1.16	1.59	0.87	1.09	0.62	0.84	1.22	1.61	1.28
	Er	10.94	8.02	2.70	3.22	1.79	2.51	1.56	1.99	2.59	4.26	2.99
	Tm	1.41	1.06	0.41	0.46	0.29	0.40	0.24	0.29	0.24	0.67	0.44
	Yb	7.95	5.37	2.39	2.73	1.74	3.07	1.48	1.91	1.83	5.56	2.49
	Lu	1.05	0.79	0.31	0.45	0.29	0.47	0.23	0.27	0.27	0.82	0.45
	ΣREE	811.02	763.69	404.18	446.68	286.03	319.42	187.78	376.81	627.06	433.35	421.38
	Sr/Ba	0.072	0.092	0.226	0.235	0.203	0.415	0.182	0.299	0.585	0.335	0.355
	Zr/Hf	50.695	40.053	32.311	25.902	32.938	32.907	32.686	40.349	34.798	37.54	35.257
	Nb/Ta	10.486	5.667	6.988	2.447	4.981	6.387	2.623	4.684	2.90	9.22	5.552
	Th/U	1.596	2.786	4.542	4.657	4.508	4.908	5.354	3.413	4.638	5.479	2.515

 Table 4. Content of trace and rare-earth elements in alkaline rocks of the Svidnya association, ppm

 Таблица 4. Съдържание на редки и редкоземни елементи в алкални скали от Свидненската асоциация, ppm



Fig. 5. Variation of some chemical components and the agpaitic coefficient Ka versus MgO or the Mg # = 100 Mg/(Mg + Fe), for rocks of the different magmatic phases (I-IV)

Фиг. 5. Вариации на някои химични компоненти и коефициента на агпаитност Ка спрямо MgO или Mg # = 100Mg/(Mg + Fe), за скали от различните магматични фази (I-IV)

REE

The content of rare earth elements (REE) in some rock types of the Svidnya magmatic association is present in Table 4. Chondrite normalized patterns (Sun, McDonougt, 1989) of distribution are illustrated in Fig. 7. In all shonkinites and syenites the different REE show similar behaviour, with the light REE exceeding the heavy REE, with an insignificant Eu anomaly, and approximately equal inclination of the lines. These features are indicative of the genetic affiliation and homodromous evolution of all main rocks. Higher REE con centrations and negative Eu anomaly are are typical only of the early pyroxenites, in



Fig. 6. Variation in some trace elements (Zr, Y, Nb, Ta; Th, U, Hf) compared to SiO₂ content and Mg # = 100Mg/(Mg + Fe), for rocks of the different phases, in ppm Фиг. 6. Вариации на някои елементи-примеси (Zr, Y, Nb, Ta; Th, U, Hf), в сравнение със

Сил. 6. Вариации на някой елементи-примеси (Zr, Y, No, 1a, 1n, U, H1), в сравнение със съдържанието на SiO₂ и Mg # = 100 Mg/(Mg + Fe) за скали от различните фази, в ppm

opposite to the lower concentration and a positive Eu anomaly in the carbonate rocks (Fig. 7c). Generally, the content of the heavy REE compared to the light REE gradually decrease during the differentiation process. Slight increase is seen only in its end at few latest dykes (e.g. sample No 52).

One possible explanation of the complementarily in composition of these phases can be due to splitting of a carbonate (carbonatite) liquid from the biotite pyroxenite magma in an early stage. Accumulated during the main crystallization such magma could form own bodies only in the latest episode of differentiation.



Fig. 7. Chondrite normalized REE patterns of biotite pyroxenites and glimmerites (asterisks), shonkinites (squares), syenites (circles), and carbonatites (diamonds), in ppm

Фиг. 7. Нормализирани по хондрит криви на редкоземните елементи при биотитови проксенити и глиммерити (звезди), шонкинити (квадратчета), сиенити (кръгчета) и карбонатити (ромбове), в ppm

Conclusions

The presented new chemical and petrological data confirmed the view that the magmatic rocks of the Svidnya region belong to the potassic-alkaline series.

Some new rock types have been established: biotite pyroxenites and glimmerites (with gradual transitions to shonkinites), amphibole-biotite shonkinite, amphibole syenite, clinopyroxene-biotite syenite as well as carbonatites (?).

• During the process of magma differentiation the following general sequence of rocks was formed: biotite pyroxenites and glimmerites - shonkinites - agpaitic syenites and quartz syenites - carbonate rocks.

• Some variations and trends in the chemical and petrological evolution and magma differentiation are established, namely: variations in SiO₂ (36 to 67 wt.%), in Na₂O (0.24-5.29 wt.%), in Mg# (66.36 to 12.98), in agpaitic coefficient Ka = (K+Na)/A1 (0.60 to 2.16), enrichment of Zr, Hf, U and Th at the end of the differentiation process, etc.

• The rare and rare-earth elements concentrated in the pyroxenites and shonkinites, also in the highly agpaitic syenites and syenite porphyries are of potential economic significance.

• The behaviour of the main and trace elements confirms the common genesis and homodromous formation of the rocks of the Svidnya magmatic association. Nevertheless, the chemical and mineral inhomogeneity of rocks are indicative for a considerable local variability and irregularity of the processes of magma differentiation and crystallization.

• According to the chemical composition

and concentration of rare elements, the rocks of Svidnya association are similar to the potassicalkaline rocks of the Aldan Shield, very close particularly to the intrusive rocks of the lamproitic series, though and differing from the lamproites themselves, by mineral composition and textures.

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