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# New insight into petrology, geochemistry and dating of the Vejen pluton, Bulgaria

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Abstract. The Elatsite PGE-Au-Mo porphyry copper deposit in Bulgaria is genetically related to Late Cretaceous subvolcanic dykes, intruded into the host rocks of the Berkovitsa Group (Lower Paleozoic) and in the granodiorites of the Vejen pluton. The pluton consists of hornblende-biotite granodiorite and granite. Porphyritic varieties occur on some places, too. Mafic microgranular enclaves of gabbro and diorite are included often within the marginal part of the pluton. Aplitic veins and various dykes cut all intrusive rocks. The pluton is high-K calc-alkaline, metaluminous to peraluminous and LILE-enriched. Many peculiarities of the major and trace element variations are consistent with a fractionation. Geochemical diversity (REE-patterns included) supports the idea that granitoids of the Vejen pluton derived its origin from more primitive basic magma. The existence of rough layering, mafic enclaves and cumulative packets of crystals as well as the linear trends in the variation diagrammes could serve as evidence supported also magma-mixing process. The applied discriminations are equivocal. Volcanic-arc and collision-related features are found, but the chronological relationship between the granite emplacement and the regional thermo-tectonic events are compatible with referring the pluton to the transitional characteristics between late-orogenic and post-orogenic, postkinematic, short-sustained, Caledonian type post-closure (POG) granites. Rock paragenesis and mineral evolution are indicative of crystallization under moderate total pressure, high fO<sub>2</sub>, high PH<sub>2</sub>O, high activity of silica. The applied geothermometers and geobarometers yielded an estimation of the temperatures between 739 and  $770^{\circ}$ C and depths of crystallization at ~18 km, ~15 km and ~13 km. The subsolidus re-equilibrations are estimated to have occurred at 2 kbar (~5 km) and at temperatures of about 600°C. U-Pb dating on single zircons from plutonic rocks revealed an intrusion age of  $314 \pm 4.8$  Ma for the granodiorite and a mantle isotopic contribution to its magma source.

Key words: Vejen pluton, rock-forming mineralogy, geochemistry, collision-related environment, U-Pb zircon ages.

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Резюме. Медно порфирното находище Елаците, съдържащо платиноиди, злато и молибден е генетично свързано с къснокредни субвулкански дайки, внедрени във вместващите скали на Берковска група (долен палеозой) и в гранодиоритите на Веженския плутон. Плутонът е изграден от амфибол-биотитови гранодиорити и гранити. На някои места се срещат и порфирни разновидности. Мафични микрозърнести включения от габро и диорит се срещат често в периферните му части. Всички плутонични скали се секат от аплитови жили и от разнообразни дайки. Установява се, че плутонът е високо-калиев калциево-алкален, метаалуминиев до пералуминиев и обогатен на литофилни елементи с голям ионен радиус. Много от особеностите на геохимичните изменения се съгласуват с процес на фракциониране. Геохимичното разнообразие (включително и моделите на редкоземното разпределение) подкрепят идеята, че в произхода на плутона е въвлечена и по-примитивна базична магма. Наличието на грубо разслояване на места, на мафични включения,

кумулативни пакети от кристали и неравновесни парагенези, както и на линейни трендове във вариационните диаграми могат да са доказателство и за процеси на смесване и минглинг. Приложените дискриминации са нееднозначни. Изведени са вулканско-дъгови и свързани с колизионна обстановка особености, но хроноложките взаимоотношения на вместването на гранитоидите с регионалните термо-тектонски събития са в полза на отнасянето им към преходни обстановки между късно-орогенните и пост-орогенните гранити, които са пост-кинематични и от Каледонски тип. Скалните парагенези и минераложката еволюция са показателни за кристализация при умерено общо налягане, висока  $fO_2$ , високо  $PH_2O$ , висока активност на силиция. Приложените геотермометри и геобарометри дадоха една оценка за температурата по време на кристализацията между 730 и 770°C и при дълбочини на кристализацията при ~18 km, ~15 km и ~13 km. Субсолидусните преуравновесявания са станали при налягане от 2 kbar (~5 km) и при температура от около 600°C. Възрастта на вместване на плутона е оценена по U-Pb данни от единични сепарирани циркони от гранодиорита на 314 ± 4.8 Ma. Доказан е и изотопен мантиен принос към източника на родоначалната магма.

#### Introduction

Situated in the central ridge of the Stara Planina Mts the Vejen pluton represents one of the late tectono-magmatic events of the Variscan orogeny in the Balkan tectonic zone. It is an essential element of the plutonic belt called "Stara Planina Calc-alkaline Formation" by Dimitrov (1939). Petrology, geochemistry and isotopic age of plutonic rocks are not well studied, no matter that the pluton is one of the important hosts of the PGE-Au-Mo copper ores. The mineralizations of one of the largest operating open pit copper mine Elatsite are emplaced partly within the granitoids of the Vejen pluton. Neither geochemical analyses, nor contemporary petrological and isotopic data are published for these rocks.

We present here some of our new results obtained during the work on the SCOPES Project 2000-2002, devoted to the petrology and geochemistry of the Elatsite ore deposit, with the hope that they will aid the inter-regional correlation and will help in elucidation of the magmatic history of the area. The aims of the paper are to cast a glance at the rock-forming mineralogy, to evaluate the variation in the rock geochemistry and to contribute to high precision radiometric dating of the plutonic rocks. All presented new data could add some support to the ideas about the magma genesis of the pluton studied and we believe they will be helpful in any new attempts for careful and detailed examination of the magmatism in the area.

## **Geological background**

The Vejen Pluton as one of the many intermediate and acid plutonic bodies widespread in the Balkan tectonic units (Bonchev, 1971) is a part of the Pre-Mesozoic Basement of the West-Balkan Tectonic Zone (Ivanov, 2002). It intrudes a heterogeneous rock association (Fig. 1), which is a mixture between products of oceanic crust (ensimatic island arc-derived rocks and ophiolitic fragments) and continental crust-produced rocks (Haydoutov, 1991). During the Early Paleozoic time the sequence, known in Bulgaria as a "Diabase-Phyllitoid Complex" (DFC) or Berkovitsa undivided Group (Haydoutov et al., 1979; Haydoutov, 1987) has experienced low-pressure type metamorphism in green-schist facies. The Berkovitsa Group consists of phyllites, diabases, chlorite and actinolite schists, greywackes and sandstones with island-arc affinity. The rocks of the pluton cut and contactmetamorphosed not only the greenschist metasediments and metadiabases, but also diaphtorized high-degree metamorphites. Biotitefeldspar and hornblende hornfelses and contact amphibolites, actinolite and two-mica andalusite-cordierite schists were formed around the pluton. (Trashliev, 1961). The terrigenous of Upper Carboniferous and of Permian age lie transgressively on the rocks of the DFC and of the Vejen Pluton (Kamenov, 1936; Kujkin, Milanov, 1970). The Mesozoic cover formations include Triassic, Jurassic and Cretaceous



Fig. 1. Schematic geological map of the Vejen pluton (an author's compilation from the geological maps of Bulgaria in scale 1:500 000 and 1:100 000, (1989) and from Nikolaev (1947), Trashliev, Trashlieva (1964), Kujkin, Milanov (1970), Antonov (1976), Moev, Antonov (1978) and personal observations) Фиг. 1. Схематична геоложка карта на Веженския плутон (авторска компилация по геоложките карти на България в мащаби 1:500 000 и 1:100 000 (1989) и от Николаев (1947), Трашлиев, Трашлиева (1964), Куйкин, Миланов (1970), Антонов (1976), Моев, Антонов (1978) и лични наблюдения)

sediments in continental shallow-deposited marine facies (Nikolaev, 1946; Moev, Antonov, 1978). The Mesozoic sediments of the southern limb of the Central Balkan anticline (Bonchev, 1971) are totally sliced up by the Kashana Nappe or are assimilated by Elatsite minor intrusions (Trashliev, 1961; Trashliev, Trashlieva, 1964; Kujkin et al., 1971). The timing of the nappe tectonics is fixed by the relationships with folds and the faults in the area (Antonov, 1976) to the initial stages of Austrian Orogeny in post-Turonian times. The structural picture of the localization of the porphyry copper deposit Elatsite is discussed by Kalaidzhiev et al. (1984). Some new data about the geochronology, magmatism and ore genesis in the area are presented by von Quadt et al. (2002).

#### **Petrology and rock-forming mineralogy**

The Vejen pluton is an almost homogeneous and voluminous plutonic body, composed mainly by structureless equigranular granodiorite and granite (Fig. 2). Porphyry rocks and some quartz-diorite and quartz-monzodiorite varieties occur rarely. Mafic microgranular rounded enclaves are included often in the southern marginal part of the pluton, some of them showing preserved from re-crystallization chilled rims. They are composed of hornblende gabbro, hornblende diorite and monzodiorite and could be understood as a field evidence for magma mingling and magma mixing. Rough layering and cumulative packets of crystals are observed on some places also.

The coarse-grained rocks of the Vejen pluton have colour index between 6 and 25 %.



Fig. 2. Modal composition of Vejen plutonites (Le Maitre et al., 1989): Md- monzodiorite; QMd – quartz-monzodiorite; Gd – granodiorite; MG – monzogranite. The fields of the mafic enclaves, even-grained granitoids and aplites are outlined Фиг. 2. Модален състав на Веженски плутонити

(Le Maitre et al., 1989): Md- монцодиорит; QMdкварц-монцодиорит; Gd – гранодиорит; MG – монцогранит. Очертани са полетата на мафичните включения, равномернозърнестите гранитоиди и аплити

Megascopically granitoid rocks have widely varying colours and textures related to the effects of varying crystallization conditions, as well as differences in the effects of autometasomatic and hydrothermal processes. Slightly altered granitoids are light grey or grayish-rose. With increasing effects of hydrothermal alteration, the colours change to rose, red-rose, yellow-green, or brown. Their primary paragenesis includes amphibole, biotite, plagioclase, potassium feldspar and quartz (apatite, zircon, titanite, allanite, magnetite, rutile as main accessories). The modal nomenclature (LeMaitre et al., 1989) is illustrated in the Fig. 2.

The rocks are hydrothermally altered to varying degree. The following secondary minerals are found: chlorite, sericite, epidote, albite, calcite, zoisite, kaolinite, pyrite, adularia, and quartz. The wall-rock alteration products can be referred to K-silicate type alteration (Kfeldspar-biotite metasomatites, locally prepropylitization sented). and propyliteargillization, according to the classification of Meyer and Hemley (1967). The alterations are most intensively developed around the Elatsite mine and they are connected with the evolution of the Chelopech volcano-intrusive structure.

## Feldspars

The normative anorthite composition of the plagioclases from the granodiorites and granites (Table 1) is in the range  $An_{14}$ - $An_{45}$ , while the one from mafic enclaves is  $An_{47}$ - $An_{49}$  and from aplites -  $An_9$ - $An_{15}$ . Plagioclase of the granitoids, which is the dominantly feldspar,

Table 1. Chemical composition of selected plagioclases and potassium feldspars Таблица 1. Химичен състав на избрани плагиоклази и калиеви фелдипати

Sample	Е/7-а		E/49-b		E/41-a		E/7-a	E/49-b	E/60-b	E/41-a
mineral			Plagic	clases		Potassium feldspars				
N⁰	1Pl-c	2Pl-r	13Pl-c	11Pl-r	67Pl-c	68Pl-r	2KFd	8KFd	12KFd	16KFd
SiO <sub>2</sub>	58.05	60.44	55.83	57.28	60.87	65.25	63.49	62.84	63.61	63.89
TiO <sub>2</sub>	0	0	0	0	0	0	0	0	0.06	0
$Al_2O_3$	25.96	24.70	29.28	27.79	23.92	21.84	20.30	19.91	18.93	16.85
FeOt	0.32	0	0.21	0.09	0.22	0.18	0	0	0	0.12
MnO	0	0	0.11	0.09	0	0	0	0	0	0
MgO	0	0	0	0.44	0	0	0	0	0	0
CaO	7.87	6.29	8.40	7.64	9.41	5.92	0	0	0.20	0
Na <sub>2</sub> O	7.23	8.14	5.77	6.50	5.37	6.43	1.09	2.84	0.65	0.91
$K_2O$	0.21	0.17	0.18	0.19	0.25	0.41	14.92	13.33	16.12	17.80
BaO	-	-	-	-	-	-	0.11	0.17	0	0.46
Total	99.64	99.76	100.0	99.84	100.04	100.03	99.91	99.11	99.57	100.00
				Mol	. proportio	ons				
An	37.1	29.7	47.1	38.9	48.2	32.8	0	0	1.0	0
Ab	61.7	69.4	50.5	59.9	50.3	64.5	9.9	24.4	5.7	7.1
Or	1.2	0.9	2.4	1.2	1.5	2.7	89.8	75.3	93.3	92.1
Cn	-	-	-	-	-	-	0.2	0.3	0	0.8

constitutes 37 to 60 % by volume. It is slightly zoned with a composition in the cores  $An_{35}$ - $An_{45}$  (mode at  $An_{39}$ ) while the rims are oligoclases,  $An_{20}$ - $An_{30}$  (mode at  $An_{29}$ ). Plagioclase composition in the mafic enclaves is  $An_{47}$ - $An_{52}$ (average  $An_{48}$ ) and in the aplites –  $An_{10}$ - $An_{21}$ (average  $An_{17}$ ).

Potassium feldspar (10-25 % vol.) is less common in the granitoids than plagioclase. The crystals show wavy light extinction. It usually forms fine xenomorphic grains, but sometimes may be as much as about 1-2 mm in diameter. It is orthoclase microperthite (75-97 % Or).

#### Biotite

Biotite (5-13 % vol.) is characterized (Table 2) as brown in colour, with Mg # 0.43-0.54 (average 0.48). Products of various stages of chloritization, from initial development along fissures to entire chlorite pseudomorphs, are recognizable. In pseudomorphs after biotite one commonly sees iron oxides, and sometimes also titanium oxides, leucoxene, and epidote.

#### Amphiboles

All of the amphiboles analyzed in the data set (Table 3) are calcic amphiboles according to the terminology of Leake et al. (1997). Most of them are assigned to the subdivision of magnesiohornblende (Fig. 3a). Tschermakites are specified only from the rare small crystals included in the plagioclases of the porphyry granodiorites (locality Kozi Dol). The ratio Mg # diminishes slightly from the cores (62.3 average at range of 59-63) to the rims (58.7 average at range of 57-60). The amphiboles from the granodiorite porphyry are relatively higher temperature and their ratio Mg # is 72.4 average (range 68.5-76.3). The relationship between the end-members of the magmatic amphiboles depends not only on the thermodynamic crystallization conditions, but also on the degree of differentiation progress (Deer et al., 1963; Leake, 1965; Blundy, Holland, 1990; Wones, Gilbert, 1982; Wones, 1981). That is why, one of the explanations of these

Table 2. Chemical composition of selected biotites Таблица 2. Химичен състав на избрани биотити

C 1	E.//	7	E/40.1	E/(0.1	E /4	1						
Sample	E/7-a		E/49-b	E/60-b	E/4	1 <b>-</b> a						
rock						_						
Analyses	Bt/1-c	Bt/4-c	Bt/6-c	Bt/12-c	Bt/20-c	Bt/21-c						
SiO <sub>2</sub>	37.06	37.75	36.19	36.03	37.32	38.01						
TiO <sub>2</sub>	2.08	2.32	2.76	2.93	2.71	2.36						
$Al_2O_3$	15.58	15.58	15.73	14.80	15.59	15.65						
FeOt	19.30	17.91	20.13	21.55	20.27	20.23						
MnO	0.65	0.58	0.54	0.35	0.30	0.28						
MgO	10.99	11.98	10.79	11.08	9.88	10.24						
K <sub>2</sub> O	9.95	9.96	9.77	9.27	9.90	9.87						
Total	95.61	96.08	95.91	96.01	95.97	96.64						
	Structural formulae based on 22 oxygen atoms											
Si	5.910	5.938	5.782	5.779	5.935	5.990						
Al <sup>IV</sup>	2.090	2.062	2.218	2.221	2.061	2.010						
$Al^{VI}$	0.836	0.824	0.742	0.575	0.861	0.894						
Ti	0.250	0.274	0.332	0.354	0.324	0.280						
Fet	2.574	2.356	2.690	2.891	2.698	2.666						
Mn	0.088	0.077	0.073	0.048	0.040	0.037						
Mg	2.613	2.809	2.570	2.650	2.334	2.405						
Ϋ́	6.361	6.340	6.407	6.518	6.257	6.282						
Х	2.024	1.999	1.991	1.897	2.010	1.984						
Mg #	50.4	54.4	48.9	47.8	46.4	47.4						

Sample	ple E/7a			E/4	9-b	E/6	0-a	Е/7-а	
Analyses	Hb <sub>1</sub> -c	Hb <sub>2</sub> -r	Hb <sub>7</sub> -c	Hb <sub>6</sub> -r	Hb <sub>13</sub> -c	Hb <sub>14</sub> -r	Hb <sub>22</sub> -m	Hb <sub>23</sub> -m	Hb <sub>4</sub> -r*
SiO <sub>2</sub>	48.00	45.87	45.27	44.23	44.67	45.66	45.11	41.76	49.67
TiO <sub>2</sub>	0.86	0.82	0.80	0.81	0.88	0.91	0.76	0.56	0.11
$Al_2O_3$	7.85	9.07	9.64	9.30	9.79	9.25	10.17	12.15	6.45
FeOt	14.74	16.92	17.44	18.21	17.57	17.78	17.30	20.16	16.80
MnO	0.77	0.86	0.67	0.56	0.76	0.65	0.60	0.75	0.81
MgO	12.20	10.79	11.43	10.89	11.11	10.47	12.47	13.11	13.77
CaO	12.36	12.07	11.30	11.41	11.20	11.66	10.03	8.11	10.16
Na <sub>2</sub> O	0.44	0.72	1.45	1.31	1.18	0.71	1.37	1.05	0
K <sub>2</sub> O	0.59	0.86	0.58	0.80	0.62	0.75	0.73	0.52	0.13
Total	97.81	97.98	98.58	97.52	97.78	97.84	98.54	98.17	97.90
	Str	uctural fo	ormulae ba	sed on the	sum of cat	ions FM=1	3 p.f.u.		
SI	7.006	6.766	6.581	6.554	6.542	6.724	6.467	6.008	7.198
Al <sup>IV</sup>	0.994	1.234	1.419	1.446	1.458	1.276	1.533	1.992	0.802
Al <sup>VI</sup>	0.357	0.343	0.233	0.178	0.232	0.330	0.185	0.068	0.300
Ti	0.094	0.091	0.087	0.090	0.097	0.101	0.082	0.061	0.012
Fe <sup>3+</sup>	0.347	0.527	0.974	0.937	1.066	0.720	1.431	2.000	0.453
Fe <sup>2+</sup>	1.452	1.560	1.146	1.319	1.086	1.470	0.638	0.060	1.261
Mg	2.654	2.372	2.476	2.405	2.425	2.298	2.664	2.811	2.974
Mn	0.095	0.107	0.083	0.070	0.094	0.081	-	-	-
$\Sigma C$	4.999	5.000	4.999	4.999	5.000	5.000	5.000	5.000	5.000
Ca	1.933	1.908	1.760	1.812	1.757	1.840	1.541	1.250	1.578
Na-M4	0.067	0.092	0.240	0.188	0.243	0.160	0.381	0.293	0
Mn	-	-	-	-	-	-	0.073	0.091	0.099
Fe	-	-	-	-	-	-	0.005	0.366	0.322
$\Sigma B$	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	1.999
Na-A	0.058	0.113	0.169	0.188	0.093	0.043	0	0	0
Κ	0.110	0.162	0.108	0.151	0.116	0.141	0.134	0.095	0.024
ΣΑ	0.168	0.275	0.277	0.339	0.209	0.184	0.134	0.095	0.024
Mg #	64.6	60.3	68.4	64.6	69.1	61.0	80.6	86.8	65.3
$Fe^{3+}/(Fe^{3+}+Fe^{2+})$	0.193	0.253	0.459	0.415	0.116	0.329	0.690	0.825	0.223

Table 3. Chemical composition of selected amphiboles Таблица 3. Химичен състав на избрани амфиболи

 $Fe^{2+}$  and  $Fe^{3+}$  of amphiboles are calculated according to Spear and Kimball (1984). The crystallochemical formulae - after Anderson and Smith (1995). c - core of the crystal; r - rim; m - small early crystallized grains,\* - sub-solidus amphiboles, calculated on the sum of cations CFM = 15

 $Fe^{2+}$  и  $Fe^{3+}$  на амфиболите са изчислени по Spear & Kimball (1984), а кристалохимичните формули - по Anderson & Smith (1995). с - ядра на кристала; г – периферия; m – малки и ранно кристализирали зърна, \* - субсолидусни амфиболи, изчислени на основата на сума от катионите CFM = 15

unusually high ratios Mg # is that these amphiboles could be remnants and traces of a highertemperature and more primitive mafic magma mixed somehow with the acid one.

The strong correlations between the ratio Mg # and Si, Al, Ti, and alkalis are disturbed in the rims of some of the amphiboles. In such cases the amphiboles show higher Mg # ratio in

the rims, but their contents Al, Ti, K and Na p.f.u. are lower, as Si p.f.u is higher. Obviously these amphiboles are influenced by sub-solidus fluid reworking of the rocks. These re-equilibrations affected only the peripheral ones of the amphibole crystals bringing about extraction of some of the alkalis and  $Fe^{2+}$  and contributing to their more silicic composition.



Fig. 3 a. The nomenclature of amphiboles from the Vejen pluton in the classification diagramme of Leake et al. (1997); b.  $(Na + K)_A$  vs. Si p.f.u. diagramme for amphiboles of the pluton

Фиг. 3 а. Номенклатура на амфиболите от Веженския плутон в класификационната диаграма на Leake et al.(1997); b. Диаграма  $(Na + K)_A$  - Si p.f.u. за амфиболи от плутона

The average Mg # ratio in the peripheral zone in these cases reaches up to 66, whereas in the central cores it is still around 62. According to Spear (1981) and Apted and Liou (1983), the re-equilibration of the amphiboles is possible in the sub-solidus cooling to 400-600°C.

The variation of Al in the amphiboles is a function of the alkalinity of the parental magma, the primary concentration of Al in these magmas and of the total pressure during the crystallization (Hammarstrom, Zen, 1986; Hollister et al., 1987; Schmidt, 1992; Johnson, Rutherford, 1989; Thomas, Ernst, 1990). The average (Na+K)<sub>A</sub> values in the amphiboles could serve as an indirect estimation for the alkalinity of their magma (Fig. 3 b). The calculated average values of this sum for the cores are 0.275 and for the rims - 0.366 and they are indicative for the higher alkalinity in the later stages of crystallization. The alkalinity of the cores in the porphyry amphiboles from some of the granodiorites is close to the earlier stages of crystallization – average  $(Na + K)_A$  is 0.282. As a whole, the alkalinity of the main magma of the Vejen Pluton, deduced from these data seems as moderate to weak.

<sup>IV</sup>Al substitution of Si in the tetrahedron position of amphiboles is principally a function of temperature (Blundy, Holland, 1990; Anderson, Smith, 1995) and of the primary overeutectic concentration of Al and Ca in their magmas. The considerably higher average <sup>IV</sup>Al in the porphyry amphiboles from the granodiorite porphyry (<sup>V</sup>Al 1.691) comparing with the average <sup>IV</sup>Al for the amphiboles from the main granodiorite-granite body of the pluton (1.204 in the cores and 1.169 in the rims) is remarkable. It reveals that not only the porphyry amphiboles have been higher of temperature, but also it is an evidence for the relative richness of plagioclases with intermediate composition in their cores, which is indicative for the fingerprint of a higher in Ca and Al partial magma side by side with the acid one. Postmagmatic re-equilibrated rims of some amphibole crystals are <sup>IV</sup>Al-poor and they are easily identified by their patchy texture. These subsolidus amphiboles are not widespread and they have been omitted in geobarometric and geothermometric estimations.

The <sup>VI</sup>Al contents in the amphiboles generally decrease with the differentiation. These contents are perceived usually as an indicator of the crystallization pressure (Leake, 1965; Raase, 1974; Thomas, Ernst, 1990), but they could be a result of influence of activity of Si  $(a_{\rm Si})$ , as well as of the degree of polymerization of the magma. Significant differences in the crystallization conditions (total pressure,  $a_{Si}$ , and the degree of polymerization of the melt) are not supposed between the inner and the outer zones of the amphibole crystals (<sup>VI</sup>Al is 0.315 at range 0.230-0.280). On the background of the total high Al content (directly related with the crystallization pressure), the porphyry amphiboles from some granodiorite varieties are distinguished for their low contents of <sup>VI</sup>Al p.f.u. (average is 0.222 at range 0.148 to 0.231). This fact is in favour of the



Fig. 4. Amphiboles from the Vejen pluton in the diagramme <sup>IV</sup>Al vs. (<sup>VI</sup>Al + Fe<sup>3+</sup> + 2Ti<sup>4+</sup> + A-site) Фиг. 4. Амфиболи от Веженския плутон в диаграмата <sup>IV</sup>Al - (<sup>VI</sup>Al + Fe<sup>3+</sup> + 2Ti<sup>4+</sup> + A-site)

conclusion that the parental magma of the granodiorite porphyry rocks (which is taken as a whole with the same or even lower  $a_{\rm Si}$ ) had crystallized at lower degree of polymerization, comparing to the main body of the evengrained granodiorites. We could suppose that the logical reason was the relatively higher  $PH_2O$  of this partial more mafic magma, differing in the other crystallochemical peculiarities of its amphiboles, as well.

The main mutually related substitutions in the amphiboles of the Vejen pluton are some combinations of tschermakite and edenite type of exchange. Plot of the sum ( $^{VI}Al + Fe^{3+} +$  $2Ti^{4+} + A$ -site) versus  $^{IV}Al$  shows strong positive correlation of near unit slope (Fig. 4), which is in line with such a combination of substitutions. The slight excess of charges in the octahedral sites could be balanced eventually by replacements of the type Ti-richterite and Ti-riebeckite, but they obviously did not play very essential role. The relative significance of each of the main substitutions in the amphiboles studied is demonstrated well in Figs. 5 and 6.

Ti p.f.u. in the amphiboles diminishes systematically from the central cores of the



Fig. 5. Amphiboles from the Vejen pluton in the diagramme  ${}^{IV}Al + (Na + K)_A$  vs. Si p.f.u. Фиг. 5. Амфиболи от Веженския плутон в диаграмата  ${}^{IV}Al + (Na + K)_A$  - Si p.f.u.

grains to their rims, confirming that  $TiO_2$  in calcium amphiboles increases almost exclusively as a function of temperature (Ernst, Liu, 1998). The Ti-tschermakite exchange is responsible for the important part of the equilibration of their charges, as it is evidenced in



Fig. 6. Composition of amphiboles from the Vejen pluton in the diagramme  $(Na + K)_A vs. {}^{IV}Al$ Фиг. 6. Състав на амфиболи от Веженския плутон в диаграмата  $(Na + K)_A - {}^{IV}Al$ 

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Fig. 7. The different trends of the fields outlined for the amphiboles, included in plagioclases from the porphyry type granodiorite and the ones of the amphiboles from the main plutonic body testify to the genetic heterogeneity of these rocks.

The relationship between <sup>VI</sup>Al and Ti in the amphiboles (Fig. 8) is typical for the calcalkaline rocks. The delineation of the field of these series is done using the data of Deer et al. (1963), Leake (1965) and Pitcher et al. (1985).

Fig. 9 shows hornblende compositions in format to test the role of Tschermak exchange. On the basis of the data portrayed in Fig. 9 and using the experimental calibration of Schmidt (1992), we suggest that the amphibole rims indicate pressures ranging from 1 to 5 kbar. These data confirm a polybaric crystallization of the parental magmas.

The zoning of the amphiboles is accentuated by the tracing of the abundances of Si p.f.u. Average Si p.f.u. in the cores is 6.793 (range 6.579-7.145) and in the rims – 6.831 (range 6.649 – 7.309). The rather wide range of the <sup>IV</sup>Si p.f.u. in the peripheral zones proves the availability of different degrees of sub-solidus re-equilibration in the presence of Si- rich fluids, probably related to Late Cretaceous magmatism in the area. During the postmagmatic



Fig. 7. Amphiboles from the Vejen pluton in the diagramme <sup>IV</sup>Al vs. Ti p.f.u.

Фиг. 7. Амфиболи от Веженския плутон в диаграмата  ${}^{IV}Al$  - Ti p.f.u.



Fig. 8. Amphiboles from the Vejen pluton in the diagramme <sup>VI</sup>Al vs. Ti p.f.u.

Фиг. 8. Амфиболи от Веженския плутон в диаграмата <sup>VI</sup>Al - Ti p.f.u

history of the rocks the higher abundances of Si are not function of the differentiation progress, put into effect at higher potential of Si in the residium melts, as the case was in the magmatic amphiboles, but are substantiated by the acid character of the hydrothermal fluids.

The mineral assemblage of the Vejen rocks (including potassium feldspar + magnet ite) requires that mafic mineral Fe/(Fe + Mg) ratio is controlled by intensive parameters (Wones, 1981). Variations in temperature,  $fH_2O$ , and total pressure are important, but  $fO_2$  is that exerts the strongest control on silicate mineral chemistry (Anderson, Smith, 1995).

With increasing  $fO_2$ , the Fe/(Fe + Mg) ratio of the amphibole markedly decreases, independent of the Fe/Mg ratio of the whole rock. Our amphiboles fall in the field of the high  $fO_2$ plutons on the <sup>IV</sup>Al vs. Fe/(Fe + Mg) ratio plot of Anderson and Smith (1995). Calculated Fe<sup>3+</sup>/(Fe<sup>2+</sup> + Fe<sup>3+</sup>) ratios in the grains of hornblende, based on 13 cations and charge balance show that the predominant part of the amphiboles are clustered around the Fe<sup>3+</sup>/(Fe<sup>2+</sup> + Fe<sup>3+</sup>) ratio range between 0.10 and 0.45 with clear positive correlation between this ratio and the Mg # ratio. Interesting fact is that the distribu-



tion of the  $Fe^{3+}/(Fe^{2+} + Fe^{3+})$  ratios in the data set is not homogenous. The second maximum in these ratios in the range of 0.60 to 0.80 corresponds to the amphiboles with the highest Mg # ratio from the early hornblendes of the porphyry granodiorites. The crystallized at higher oxidation conditions amphiboles of these porphyry amphiboles apparently have been crystallized from different parental, not only more mafic, but also more oxidized magma. The mixing of different magmas left traces in the crystal chemical peculiarities of the amphiboles crystallized in the Vejen pluton.

## **Intensive variables**

Fig. 9. Composition of hornblendes in terms of (<sup>VI</sup>Al +  $^{IV}$ Al) vs. Si + R<sup>2+</sup>. Dashed lines are isobars based on the calibration of Schmidt (1992)

Фиг. 9. Състав на амфиболи на диаграмата (<sup>VI</sup>Al + <sup>IV</sup>Al) - Si. Щрихираните линии са изобари, изчислени по калибровката на Schmidt (1992)

The applied geothermometer (Blundy, Holland, 1990) yielded an estimation of the crystallization temperatures between 730 and 770°C (Fig. 10). The geobarometer of Anderson and Smith (1995) is applicable for Vejen plutonic rocks



Fig. 10. *P-T* conditions of crystallization, estimated from amphibole-plagioclase pairs (Anderson, Smith, 1999; Blundy, Holland, 1990). Specimen 60-a is from porphyry granodiorites and all other points are from even-grained granodiorites. Filled squares – average estimates from magmatic amphiboles; the empty square – average result from subsolidus re-equilibrated pairs. Filled circles – cores, open circles – rims. Wet tonalite solidus line is after Anderson and Smith (1995)

Фиг. 10. *P-T* условия на кристализация, оценени от амфибол-плагиоклазови двойки (Anderson, Smith, 1999; Blundy, Holland, 1990). Образец 60-а е от порфирни гранодиорити, а всички останали – от равномернозърнести гранодиорити. Плътни квадрати – среден резултат от оценките за магматичните амфиболи; празен квадрат – среден резултат от субсолидусно преуравновесени двойки; запълнени кръгчета – ядра, празни кръгчета – периферия. Линията на мокрия тоналитов солидус е по Anderson & Smith (1995)



Fig. 11. Plutonic rocks from the Vejen pluton in the plot SiO<sub>2</sub> vs (Na<sub>2</sub>O + K<sub>2</sub>O) (Bogatikov et al., 1981). Rock families: Gb – gabbro; MGb – monzogabbro; D – diorite; Qd – quartz-diorite; QMd – quartzmonzodiorite; Gd – granodiorite; QS – quartz-syenite; Gr – granite; MG – monzogranite; LGr – leucogranite Фиг. 11. Плутонични скали от Веженския плутон в диаграмата SiO<sub>2</sub> - (Na<sub>2</sub>O + K<sub>2</sub>O) по Богатиков и др. (1981)

rocks as the mineral assemblage is similar to the experimental one and the obtained temperatures are close to the isothermal granitic solidus. Selected amphibole-plagioclase pairs are used and the results are illustrated in Figs. 9 and 10. The prevailing part of the cores of the amphiboles from the plutonic rocks recorded pressures around 5 kbar, the average result being 5.3 kbar at 766 $\pm$ 30°C. Pressures about P =3.9 kbar are calculated for the rims of the magmatic amphiboles. At  $d_v = 2.75$  t/m<sup>3</sup>, the depth of the outset of the amphibole crystallization was around 12 km and the level of the end of this process was at about 10 km at temperature of 732°C. The porphyry amphiboles started their crystallization at a deeper magma level (P 6.1 kbar at 755°C). The last subsolidus re-equilibration in some of the amphibole rims was at P 2.25 kbar at 665°C. It means that then the pluton has already been uplifted to the levels close to 5.0-5.5 km. It is very probable the subsolidus alteration of the amphiboles to be connected with the Late Cretaceous fluid systems, superimposed their influence on the already crystallized for a long time ago Vejen pluton. The rather wide range of the pressure estimates (Fig. 10) is evidence that the crystallization of the plutonic rocks was progressing simultaneously with the rising of the magma.

# Geochemistry and geodynamic setting

The whole-rock silicate analyses (Table 4) plotted on the diagramme ( $Na_2O + K_2O$ ) vs. SiO<sub>2</sub> (Bogatikov et al., 1981) are demonstrated in Fig. 11. The rocks fall almost entirely within the high-K calc-alkaline series (Peccerrillo, Taylor, 1976) and partly to the calc-alkaline series (Fig. 12). Metaluminous to peraluminous character of the granitoids is established. Peacock's index is 58. Selected variation

Sample	E/45-a	E/46-v	E/7-a	E/44-v	E/20	E/54	E/13	E/41-d	E/45-b	E/60-b
Туре	Encla	aves		Main	plutonic	body		Apli	ites	Porph.
SiO <sub>2</sub>	51.19	54.38	58.79	61.48	63.26	66.33	67.74	72.52	76.79	62.86
TiO <sub>2</sub>	0.69	0.77	0.42	0.66	0.78	0.58	0.63	0.24	0.07	0.79
$Al_2O_3$	15.93	17.23	16.91	14.60	13.42	12.83	13.43	12.45	11.76	14.29
$Fe_2O_3$	2.98	3.98	2.58	2.36	3.31	1.93	1.65	0.66	0.78	1.94
FeO	6.71	5.41	2.31	4.57	3.20	3.62	2.69	3.30	0.60	4.12
MnO	0.40	0.26	0.18	0.20	0.17	0.18	0.11	0.21	0.06	0.18
MgO	6.46	3.60	2.25	3.55	3.15	2.75	2.53	0.94	0.63	3.14
CaO	7.72	4.99	5.60	4.90	3.77	4.32	2.40	1.01	1.03	3.64
Na <sub>2</sub> O	3.10	3.10	4.30	3.23	2.76	2.91	3.05	3.23	3.18	3.07
$K_2O$	1.58	3.04	3.76	2.94	3.18	2.66	3.41	5.52	4.09	3.01
$P_2O_5$	0.26	0.25	0.31	0.26	0.22	0.34	0.22	0.13	0.05	0.29
$H_2O^-$	0.14	0.10	0.24	0.06	0.10	0.14	0.13	0.16	0.04	0.14
L.O.I.	2.85	2.78	0.99	1.64	1.80	1.01	1.76	0.20	0.34	1.90
Total	100.01	99.69	99.68	99.87	99.61	99.61	99.75	100.57	99.42	99.65
q	-	6.82	3.94	15.18	23.03	26.29	27.95	27.07	39.81	20.02
or	9.63	18.54	16.98	17.60	19.35	15.98	20.61	32.58	24.43	18.29
ab	27.00	27.01	45.47	27.63	23.99	24.98	26.34	27.24	27.14	26.66
an	25.61	24.02	15.26	16.82	15.22	14.27	10.85	3.12	4.87	16.73
Di(wo)	5.14	-	4.74	2.61	1.13	2.29	-	0.47	-	0.04
Di(en)	3.07	-	2.92	1.51	0.80	1.33	-	0.15	-	0.02
Di(fs)	1.80	-	1.54	0.98	0.20	0.85	-	0.34	-	0.01
С	0	0.29	0	0	0	0	0.83	0	0.33	0
hy (en)	13.22	9.28	2.62	7.48	7.30	5.66	6.46	2.20	1.59	8.04
hy (fs)	7.73	6.03	1.38	4.89	2.01	3.64	2.80	5.15	0.46	5.11
ol (fo)	0.25	0	0	0	0	0	0	0	0	0
ol (fa)	0.16	0	0	0	0	0	0	0	0	0
mt	4.45	5.95	3.16	3.46	4.94	2.84	2.44	0.95	1.14	2.89
ilm	1.35	1.51	1.07	1.27	1.52	1.12	1.22	0.46	0.13	1.54
hem	0	0	0	0	0	0	0	0	0	0
ap	0.59	0.56	0.62	0.57	0.49	0.75	0.49	0.28	0.11	0.65
An %	48.7	47.1	25.1	36.63	38.8	36.4	29.2	10.3	15.2	38.6
Σ P1	52.61	51.03	60.73	44.45	39.21	39.25	37.19	30.36	32.01	43.39
М	37.8	23.6	18.0	22.8	18.4	18.5	14.2	10.0	3.8	18.3
F.I.	62.24	76.39	81.65	77.2	81.59	81.52	85.75	90.01	96.25	81.7
Norm. rock	Md	QMd	Md	QMd	Gd	Gd	Gd	MG-apl	MG	Gd
Chem. rock	D	QMd	QMd	Qd	Qd	Gd	Qd	G-apl	LGr	Gd

Table 4. Selected chemical compositions and CIPW norms of rocks from Vejen pluton Таблица 4. Избрани химични състави и СIPW норми на скали от Веженския плутон

1. The analyses are performed in the Chemical Laboratory of Sofia University, Faculty of Geology and Geography by the analysts E. Landjeva and K. Krasteva. 2. M - mafic index; F.I. – Larsen's felsic index. 3. Norm. rock means the nomenclature using the normative composition and Chem. Rock – the same using the SiO<sub>2</sub> vs. (Na<sub>2</sub>O + K<sub>2</sub>O) -classification (Bogatikov et al., 1981). 4. The abbreviations are as follows: D – diorite, Md – monzodiorite, QMd – quartz-monzodiorite, Qd – quartz-diorite, Gd – granodiorite, MG – monzogranite, LGr – leucogranite, G-apl – granite-aplite, MG-apl – monzogranite-aplite, Porph. – porphyry granodiorite from the locality Kozi Dol

1. Анализите са изпълнени в Химичната лаборатория на ГГФ на СУ от аналитиците Е. Ланджева и К. Кръстева. 2. М – мафичен индекс; F.I. – фелзичен индекс на Ларсен. 3. Norm. госк означава номенклатурата с използване на нормативния състав, а Chem. Rock – същото при прилагане на диаграмата SiO<sub>2</sub> vs. (Na<sub>2</sub>O + K<sub>2</sub>O) на Богатиков и др. (1981). 4. Другите съкращения са както следва: D – диорит, Md – монцодиорит, QMd – кварц-монцодиорит, Qd – кварц-диорит, Gd – гранодиорит, MG – монцогранит, LGr – левкогранит, G-аpl – гранит-аплит, MG-аpl – монцогранит-аплит, Porph. – порфирен гранодиорит от местността Кози дол



Fig. 12.  $K_2O$  vs. SiO<sub>2</sub> plot (Peccerillo, Taylor, 1976) expanded (dotted lines) by Dabovski et al. (1989). Series: TH – tholeiitic; CA – calc-alkaline; h-K CA – high-potassium calc-alkaline; SH – shoshonitic, u-kSH – ultra-high-K shoshonitic

Фиг. 12. Диаграма K<sub>2</sub>O - SiO<sub>2</sub> (Peccerillo, Taylor, 1976), разширена по щрихираните линии от Dabovski et al. (1989). Серии: TH – толеитова; CA – калциево-алкална; h-K CA – високо-калиево калциево-алкална; SH – шошонитова u-kSH – ултра-калиева шошонитова

diagrammes for major and trace elements (Table 5) are present (Fig. 13). These Harker's variations reveal sub-linear trends of decreasing TiO<sub>2</sub>, MgO, CaO, Fe<sub>2</sub>O<sub>3</sub>, MnO, Al<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, Sr (Fig. 12) and of Zr, Sc, Co, Zn, Hf, Y, La, Ce (not shown). K, Na, Ta, Nb, Th behave as incompatible elements. Oxide and element variations are broadly along extrapolations of typical calc-alkaline trends. The petrographical, mineralogical and geochemical criteria (Chappell, White, 1974; Pitcher, 1983; Atherton, Tarney, 1979) point to the assignment of the granitoids to the I-type (Caledonian subtype).

Ocean-ridge-granite-normalized spidergrams (Fig. 14) are typical for calc-alkaline orogenic granites (Pearce et al., 1984). The negative Nb-Ta anomalies in these diagrammes are characteristic features of subduction-related magmatic rocks. The residium of leucocratic granitic composition is also directly observed in the aplitic veins.

Chondrite-normalized REE distributions are presented in Fig. 15. They resemble closely those of typical island-arc calc-alkaline rocks with LREE-enriched to HREE-depleted and flat patterns. The weak degree of differentiation of the HREE possibly is explained by weak enrichment of the magma source. We should emphasize the negative correlation between  $La_N$  and SiO<sub>2</sub>, which is a feature, which is not in line with island-arc signature. All patterns exhibit moderate to large negative Eu anomalies, demonstrating that the plagioclase-bearing sources of melting have not been very deep.

Rb vs. Sr correlation for the granitoids (Fig. 16) is juxtaposed with some vectors of fractionation, calculated for different degrees (F=0, 0.2 and 0.4). The negative correlation could be explained by a combined fractionation of feldspars. The Rb/Sr ratio increases with the fractionation (Fig. 17). The involvement of biotite and plagioclase in the magma evolution is indicated by such a correlation. Amphibole fractionation might have been theoretically responsible for the trend in Fig. 18 with Yb vs. La/Yb relationship. The increasing of La/Yb ratio with decreasing of Yb would necessitate a fractionation of unrealistically large amounts of

Sample	Е/7-а	E/44-v	E/20	E/54	E/51-a	E/13	E/41-d	E/45-b	E/60-b
Туре		Ν	/lain plut	onic body			Apl	ites	Porph.
Cr	32	59	43	83	76	61	80	27	81
Ni	13.7	25.4	11.3	10.9	20.3	16.6	46	6.8	17.6
Со	10.2	15.6	15.4	13.6	12.9	18.6	7.2	1.5	17.7
Sc	11	16	19	18	16	17	4	2	20
Y	18.3	22.9	28.0	27.6	25.1	28.9	15.2	17.9	31.0
Nb	5.3	13.0	13.5	10.6	11.1	11.0	11.7	15.9	13.7
Zr	109	185	210	356	192	191	89	61	267
Hf	2.9	4.9	5.4	9.2	5.5	4.9	2.8	3.7	6.6
Cu	239	72	19	22	23	17	41	12	23
Zn	40	63	78	57	52	43	23	12	79
Mo	2.0	5.8	1.7	2.2	1.1	1.8	12.3	2.1	2.4
Sr	983	347	291	239	242	285	179	46	310
Ba	696	726	875	408	633	984	732	89	799
Rb	80	109	124	101	122	117	184	267	123
Та	0.32	1.02	0.97	0.90	0.99	0.90	1.37	3.56	1.25
Pb	11.2	25.5	23.9	16.3	23.1	17.7	20.3	36.8	27.3
Th	11.3	16.4	16.8	30.2	25.0	20.5	22.3	24.0	20.8
U	3.5	5.0	3.2	8.8	5.7	5.6	7.0	7.5	7.9
La	41.05	41.16	45.10	48.05	39.21	43.06	25.10	10.51	47.13
Ce	69.20	72.47	82.31	89.00	72.06	75.07	44.06	22.16	85.12
Pr	7.30	7.84	8.86	9.66	7.97	8.62	4.55	2.81	9.48
Nd	28.26	28.93	34.10	34.97	28.16	32.69	15.61	9.92	37.43
Sm	4.71	5.80	6.79	6.77	4.75	5.88	2.75	2.43	8.14
Eu	1.34	1.38	1.37	1.01	0.96	1.30	0.57	0.38	1.42
Gd	3.72	4.48	5.23	5.54	4.07	5.51	2.36	2.22	6.18
Tb	0.55	0.64	0.86	0.79	0.66	0.94	0.36	0.50	0.93
Dy	3.24	4.29	5.01	4.98	4.39	4.89	2.31	2.29	5.97
Но	0.67	0.81	0.95	0.98	0.88	1.09	0.50	0.62	1.07
Er	1.92	2.14	2.57	2.77	2.16	2.56	1.49	1.84	2.95
Tm	0.28	0.37	0.43	0.34	0.41	0.43	0.28	0.34	0.49
Yb	1.99	2.04	2.82	3.08	3.97	2.92	1.70	2.11	2.98
Lu	0.29	0.36	0.44	0.45	0.39	0.46	0.28	0.50	0.49

Table 5. Trace elements in some selected fresh rocks, ppm Таблица 5. Елементи-следи в избрани свежи скали, ppm

Trace-element analyses, including REE were carried out by ICP-MS using Excimer Laser Ablation (Elan 6000) on lithium tetraborate pellets by A. von Quadt in Isotope Geochemistry and Mineral Resources, Department of Earth Sciences, ETH-Zűrich, Switzerland

Анализите на елементи-следи, включително и на редкоземните елементи са изпълнени по метода ICP-MS чрез лазерна аблация върху таблетки от литиев тетраборат и на апарат Elan 6000 от А. фон Куадт в Лабораторията по изотопна геохимия на Отдела за науки за Земята в Швейцарския технологически институт (ETH) в гр. Цюрих

amphibole ( $K_D^{Yb/Amph}$  is1.5 - 2.0!). All these plots confirm that many peculiarities of the major and trace element variations are consistent with a fractionation of an assemblage, dominated with increasing proportions of feldspars to mafic minerals.

The Ba/Nb vs. Nb correlation of the sam-

ples from the Vejen Pluton (Fig. 19) is in accord with the vector of the partial melting and not of the one for fractionation (Hofmann, 1988). High Ba/Nb ratios tend to be negatively correlated with Nb variations. If slab melts were directly involved in the petrogenesis, a possible correlation between Ba/Nb and Nb



Fig. 13. Selected Harker's diagrammes for rocks from the Vejen pluton. Symboles: circles – even-grained granitoids; squares – enclaves; triangles – aplites; diamonds – porphyry type granodiorites Фиг. 13. Избрани Харкерови диаграми за скали от Веженския плутон. Символи: кръгчета – равномернозърнести гранитоиди; квадратчета – включения; триъгълници – аплити; ромбове – порфирен тип гранодиорити



Fig. 14. ORG-normalized trace element patterns (Pearce et al., 1984) for selected fresh samples: slanting hatch – granodiorites; light overshade – aplites

Фиг. 14. Нормализирани към океанско-хребетен гранит модели на елементи-следи по Pearce et al. (1984) за избрани свежи образци: наклонена щриховка – гранодиорити; светло засенчване – аплити

should be observed, because magmas are supposed to transport Ba into the mantle wedge. Paying attention to the negative correlation between  $SiO_2$  and Yb concentrations expressed for the Vejen Pluton samples, it is supposed that a hornblende- and a plagioclase-bearing source was involved in the partial melting process. Diminishing Yb concentrations correlated with increasing  $SiO_2$  content is a well-known characteristic of the melting from amphibolite source. This lower crust material probably produced the basic magma, which interacted with acid mid-crust melts to form the granodiorites of the Vejen Pluton.

MgO vs. Al<sub>2</sub>O<sub>3</sub> (wt. %) biotite discrimination diagramme of Abdel-Rahman (1994) refers the studied samples to the orogenic calcalkaline granites (Fig. 20). A display of selected granitoid compositions (after screening to remove the altered samples) on the R1 - R2 multicationic diagramme (Batchelor, Bowden, 1985) on Fig. 21a shows that the Vejen samples straddle the division of post-collision uplift (field 3), pre-plate collision (field 2) and syn-collision (field 6), the last one being predominant. Subduction regime is also occupied with many of the samples. Rb vs. (Y + Nb)discriminant diagram of Pearce et al. (1984) is shown in Fig. 21b. The result implies volcanicarc environment. The applied Rb/30 -Tax3 - Hf discrimination diagramme of Harris et al. (1986) - Fig. 21c is typical for the volcanic-arc granites. In contrast, the contents of some HFSE (Fig. 21d, after Thieblemont, Tegyey, 1994) classify the samples mainly in the collision-related settings. Obviously the source characteristics of the Vejen granites had preserved some of the geochemical signatures of the old island-arc lower crust and they were inherited in the post-collisional process of granite-formation. The trivial discrimination geochemical methods do not work properly for the case of Vejen Pluton, as it is the case in many post-collision granites.

Partial melting of already-crystallized mafic/intermediate rocks, possibly underplated at the base of the crust during old subduction along a continental margin and a minglingmixing with acid melts crust-derived is the model proposed for the origin of the pluton.

The tectonics of the area in which emplacement occurred, the nature of associated



Fig. 15. Chondrite-normalized REE patterns (same symbols as in Fig. 14).

Фиг. 15. Хондрит-нормализирани разпределения на редкоземни елементи (същите символи както на фиг. 14)



Fig. 16. Sr vs. Rb plot with fractionation vectors for biotite (Bt), hornblende (Hb), plagioclase (Pl), and K-feldspar (KF). The proportions of fractionated minerals from a provisional parental magma are marked to produce comparable changes in the concentrations of Rb and Sr. Distribution coefficients are selected for acid melts and crystallization conditions, close to the estimated for the pluton

Фиг. 16. Диаграма Sr – Rb с вектори на фракционирането за биотит (Bt), амфибол (Hb), плагиоклаз (Pl) и калиев фелдшпат (KF). Отбелязани са пропорциите на фракциониращите се минерали от условна родоначална магма за сравними изменения в концентрациите на Rb и Sr. Коефициентите на разпределение са избрани за кисели топилки и за кристализационните условия, близки до оценките за плутона

magmatic rocks, and the temporal relationship between granite emplacement and other thermo-tectonic events in the area, in spite of the equivocal geochemical discriminations, are compatible with the classification of the pluton as transitional between late-orogenic and postorogenic granites (Rogers, 1981; Rogers, Greenberg, 1990). In fact, all geochemical variations support only the idea that a more primitive magma had been evolved in the chemical evolution of the pluton. These variations do not contradict to other processes like magma mixing, because magma mixing is the classical cause of linear variations in major and trace element Harker's diagrams. The existence of rough layering, mafic enclaves and cumulates, cumulative packets of crystals and some cores of the rock-forming minerals in disequilibria with the evolved magma could serve to support such ideas.

## **Isotope data**

U-Pb single zircon method was used for the precise geochronological dating of the Vejen pluton. Isotope-geochemical Rb/Sr-whole rock and Hf-zircon tracing provide information about the origin of the studied rocks. Detailed analytical techniques are given in Von Quadt et al. (2002).

U-Pb single zircon dating determines for the granodiorites of the Vejen Pluton (sample E/44-5, Table 6) a crystallization age of  $314 \pm$ 4.8 Ma (Fig. 22). Negligible lead losses coincide with the data for a partial re-equilibration of hornblende and plagioclase. The recent lead loss is probably connected to the Cretaceous



Fig. 17. Rb/Sr vs. Sr plot. The average composition of the geochemical I-type granite and the fractionation vectors are from Harris et al. (1986)

Фиг. 17. Диаграма Rb/Sr – Sr. Средният състав на геохимичния тип гранити I и векторите на фракционирането са от Harris et al. (1986)



Fig. 18. Yb vs. La/Yb relationships Фиг. 18. Взаимоотношения Yb vs. La/Yb

magmatic activity including the thermal overprint of the rocks. The  $\varepsilon$ -Hf<sub>(300 Ma)</sub> of the zircons (Table 7) reveals slightly negative values of – 0.96 to 0.60 which are in agreement with the geochemical evidence for a mixed crust-mantle origin of the magma.

Strontium characteristics of two chosen samples confirm the conclusion for a mixed crust-mantle origin of the Vejen granodiorites: initial <sup>87</sup>Sr/<sup>86</sup>Sr ratio at 315 Ma is 0.70896 for sample E/66-b and 0.70729 in sample E/44-5. The initial strontium ratios reflect possible isotope heterogeneity of the granodiorite magma – another argument for the mingling-mixing phenomena of the studied rocks.

The  ${}^{87}$ Sr/ ${}^{86}$ Sr ratio at Cretaceous time (90 Ma) is calculated with 0.71100 and 0.70966 respectively. This means that the Variscan



Fig. 19. Ba/Nb ratios trend (Hofmann, 1988) negatively correlated with Nb concentrations

Фиг. 19. Отрицателна корелация на тренда на отношението Ba/Nb (Hofmann, 1988) с концентрациите на Nb



Fig. 20. Biotite discrimination diagramme after Abdel-Rahman (1994) FeO vs. Al<sub>2</sub>O<sub>3</sub> (wt. %). Fields of discriminated granites: P – peraluminous; C – calcalkaline; A – alkaline

Фиг. 20. Дискриминантна диаграма FeO vs. Al<sub>2</sub>O<sub>3</sub> (wt. %) по състава на биотити (Abdel-Rahman, 1994). Полета за дискриминираните гранити: Р – свръхалкални; С – калциево-алкални; А – алкални

crust materials of the Vejen Pluton had a negligible influence on the Cenomanian dykes in the region of the Elatsite PGE-Au-Mo porphyry copper deposit (initial Sr ratio of 0.705-0.706, von Quadt et al., 2002).

#### Conclusions

1. The petrographical diversity in the Vejen Pluton includes granodiorite and granite mainly, containing abundant mafic enclaves in the marginal parts of the pluton.

2. The new isotopic data reported here provide the first persuasive evidence for its Late Carboniferous age - 314 Ma.

3. Compositional variations in the rockforming minerals have been used to interpret variations in the physical and chemical conditions, brought about the processes such as magma mixing, pressure changes and convection during crystallization. Textural and field relations also support such an idea.

4. The chemical range (major, trace and earth elements) confirm the calc-alkaline affinity of the metaluminous to peraluminous magmas, produced the plutonic rocks. Fractional crystallization could explain the chemical



HfTa x 3Zr (ppm)Fig. 21. A display of selected rocks from the Vejen pluton (after screening to remove altered samples) on<br/>some discriminant diagrammes: a. R1 – R2 multicationic diagramme (after Batchellor and Bowden, 1985); b.<br/>Rb vs. (Y + Nb) discriminant diagramme (Pearce et al., 1984); c. Rb/30 – Tax3 – Hf diagramme (Harris et al.,<br/>1986); d. Zr vs. (Nb/Zr)<sub>N</sub> discriminant plot (Thieblemont, Tegyey, 1994) with normalization to values of Nb<br/>and Zr in the primordial mantle (Hofmann, 1988). The symbols are the same as in the Fig 13.Фиг. 21. Дискриминантни диаграми на избрани скали от Веженския плутон (след отделяне на<br/>променените образци): a. R1 – R2 мултикатионна диаграма (по Batchellor & Bowden, 1985); b. Rb vs.<br/>(Y + Nb) дискриминантна диаграма (Pearce et al., 1984); c. Rb/30 – Tax3 – Hf диаграма (Harris et al.,<br/>1986); b. Rb vs.

(1 × 16) дискрыянантна диа раза (Геагес ег ал., 1961), с. 16050 – 1405 – 111 диа раза (Пать ег ал., 1986); d. Zr vs. (Nb/Zr)<sub>N</sub> дискриминантна диаграма (Thieblemont, Tegyey, 1994) с нормализация към стойностите на Nb и Zr в примитивната мантия по оценките на Hofmann (1988). Символите са същите, както на фиг. 13

variations, but partial melting and magma mixing are equally plausible models.

5. Tectonic discriminations are equivocal. Volcanic-arc and post-collision settings are equally well substantiated. The source dependence of tectonic classification implies that granitoids studied are likely to inherit apparent tectonic characteristics from their sources, regardless of the actual conditions of magma generation. We suggest that the inheritance of geochemical components from subducted older materials can produce the arc-like features revealed by some of the discriminations. The post-collision evolution of the Variscan belt was complex and is still not fully understood. Significant crustal heating and melting as a result of magma

N	Measu- rement	weight	U	Pb	<sup>206</sup> Pb/ <sup>204</sup> Pb	<sup>206</sup> Pb/ <sup>238</sup> U	$2\sigma$ error	<sup>207</sup> Pb/ <sup>235</sup>	2σ	<sup>207</sup> Pb/ <sup>206</sup> Pb	2σ	<sup>206</sup> Pb/ <sup>238</sup> U	<sup>207</sup> Pb/ <sup>235</sup> U	<sup>207</sup> Pb/ <sup>206</sup> Pb	Rho
	N	in mg	ppm	ppm	10/ 10	10/ 0	20 01101	U	error	error			apparent age	KIIO	
1	IP 30	0.0153	174.4	7.515	586.5	0.03822	0.00018	0.2756	0.0014	0.05285	0.00010	241.8	249.5	322.7	0.92
2	IP 31	0.0217	129.2	6.732	2835.5	0.04966	0.00024	0.3606	0.0020	0.05267	0.00012	312.4	312.6	314.4	0.90
3	IP 32	0.0135	223.3	9.801	498.6	0.03873	0.00022	0.2816	0.0027	0.05272	0.00040	244.9	251.9	317.1	0.62
4	IP 36	0.0247	133.6	6.922	1565.6	0.04875	0.00029	0.3545	0.0026	0.05273	0.00022	306.8	308.1	317.2	0.83

 Table 6. U-Pb isotope data for abraded zircons from granodiorite E/44-5

 Таблица 6. U-Pb изотопни данни за циркони от гранодиорити, проба E/44-5

Rho - correlation coefficient  $^{206}\text{Pb}/^{238}\text{U}-^{207}\text{Pb}/^{235}\text{U}$  Rho - коефициент на корелация  $^{206}\text{Pb}/^{238}\text{U}-^{207}\text{Pb}/^{235}\text{U}$ 

 Table 7. Hf isotope data for zircons of the Vejen pluton granodiorite (sample E/44-5)

 Таблица 7. Hf изотопни данни за циркони от гранодиорити на Веженския плутон (проба E/44-5)

No	<sup>176</sup> Hf/ <sup>177</sup> Hf	$2\sigma$ error	ε-Hf	ε-Hf Τ <sub>300 Ma</sub>
IP 31	0.282578	0.000002	-6.86	-0.60
IP 32	0.282568	0.000010	-7.21	-0.96
IP 36	0.282576	0.000006	-6.93	-0.67



Fig. 22. U-Pb isotope concordia diagramme for zircons Фиг. 22. U-Pb изотопна диаграма с конкордия за циркони

underplating, contemporary with crust extension is only supposed and the new data could add some support to the tectonic reconstructions. The Variscan orogeny produced wide spread granitoid plutons in the basement units of West Carpathians (Poller et al., 2002) as well as in various tectonic units of the Europe (the French Massif Central for example, Stemprok et al., 1997), so future correlations of Vejen pluton with the other occurrences will be useful.

6. The depth of emplacement of the pluton was relatively moderate and the prevailing temperature was close to the granodiorite solidus.

7. The supposed magma source was probably within the lower part of the crust and the tectonic regimen during the melting was extensional. Mixed crust-mantle origin was supported by the initial Sr ratios (0.708 to 0.709) and  $\epsilon$ -Hf<sub>(300 Ma)</sub>.

8. Subsolidus re-equilibrations and hydrothermal influence on the solidified rocks are well developed in the west-southern part of the pluton. There are plausible arguments that they are developed in relation with the Late Cretaceous magmatism and mineralizations widely distributed in the area.

9. The supposed involvement of mafic mantle magma in the evolution of the Vejen granitoids

could have something to do with the unique PGE-mineralizations, accompanying the main Late Cretaceous copper porphyry deposits.

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