

## PETROLOGY, GEOCHEMISTRY, SR AND ND ISOTOPE CHARACTERISTICS AND MINERAL CHEMISTRY OF THE DYKES IN THE ZLATITSA PASS, SREDNOGORIE MAGMATIC ZONE

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**ABSTRACT.** The investigated dykes are located eastern of the Chelopech volcanic complex situated in the Central Srednogorie magmatic zone which host one of the largest Cu-Au deposits in Europe. These rocks are porphyritic with plagioclase and amphibole phenocrysts, and quartz and biotite are rare. These dykes have andesitic, latitic, dacitic and trachydacitic compositions. The trace element distribution is typical for an active continental margin.

**ПЕТРОЛОГИЯ, ГЕОХИМИЯ, SR И ND ИЗОТОПНА ХАРАКТЕРИСТИКА И ХИМИЧЕН СЪСТАВ НА ГЛАВНИТЕ СКАЛООБЛАЗУВАЩИ МИНЕРАЛИ НА ДАЙКИТЕ ОТ ЗЛАТИШКИЯ ПРОХОД, СРЕДНОГОРСКА МАГМЕНА ЗОНА**  
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**РЕЗЮМЕ.** Изследваните дайкови скали са разположени източно от продуктите на Челопешкия вулкан, разположен в Централносредногорската магмена зона. В нея се намират едни от най-големите Cu-Au находища в Европа. Тези дайкови скали са порфирни по плагиоклаз и амфибол, в по-малки количества се наблюдават биотит и кварц. Те са с андезитов, латитов, дацитов и трахидацитов състав. Разпределението на елементите следи в тях е подобно, на това наблюдавано в активните континентални крайнини.

### Introduction

The investigated dykes outcropped eastern of the Chelopech volcanic complex products. They are located in the Central Srednogorie volcano-plutonic area, which forms part of the Srednogorie tectonic zone (Dabovski et al., 1991). The aim of our investigation is to reconstruct the geological evolution of the Late Cretaceous dyke complex. An important part of the present study is to trace the magmatic source, and reconstruct the magmatic processes. We have combined field observations with representative whole rock and mineral geochemical analyses. Isotope Sm-Nd and Rb-Sr whole rock analyses provide an additional information about the magma sources and their evolution.

### Geology of the region

The basement of the magmatic rocks consists of high-grade metamorphic rocks (two-mica migmatites with thin intercalations of amphibolites, amphibole-biotite and biotite gneisses), and low metamorphic phyllites and diabases of the Berkovitsa group (Early Paleozoic island-arc volcanic complex, Haydoutov, 2001). These units are in tectonic contact with each other, and to the North of Chelopech the phyllites of the Berkovitsa group are intruded by the Variscan granitoids (Kamenov et al., 2002) of the Vejen pluton. The Late

Cretaceous succession in the region starts with conglomerates and coarse-grain sandstones intercalated with coal-bearing interbeds (coal-bearing formation, Moev and Antonov, 1978) covered by polymictic, argillaceous and arcose sandstones to siltstones (sandstone formation). Collectively, these units have a thickness of less than 500 m. Pollen data suggests that both formations are Turonian (Stoykov and Pavlishina, 2003). The sedimentary rocks are cut by volcanic bodies and overlain by sedimentary and volcanic rocks of the Chelopech Formation (Moev and Antonov, 1978). It comprises the products of the Chelopech volcanic complex, epiclastics, as well as the Vozdol sandstones (Fig. 1). The latter are recently paleontologically dated as Turonian in age (Stoykov and Pavlishina, 2003). These formations have been eroded and transgressively covered by sedimentary rocks of the Upper Senonian-Campanian Mirkovo Formation (reddish limestones and marls), which is in turn overlain by flysch of the Chugovo Formation (Campanian-Maetrichtian in age, Moev and Antonov, 1978) (Fig. 1). Several dykes are exposed to the east compared to the Chelopech volcanic complex. They strike predominately in an east-west direction and intrude into the Pre-upper Cretaceous metamorphic basement. They do not show crosscutting relationship to the Chelopech volcanic complex. The largest dyke is more than 7 km in length. These dykes have andesitic, latitic, dacitic and trachydacitic compositions. Based on their structures, host rocks, crosscutting relationships and alterations the Stoykov et al. (2002, 2003,

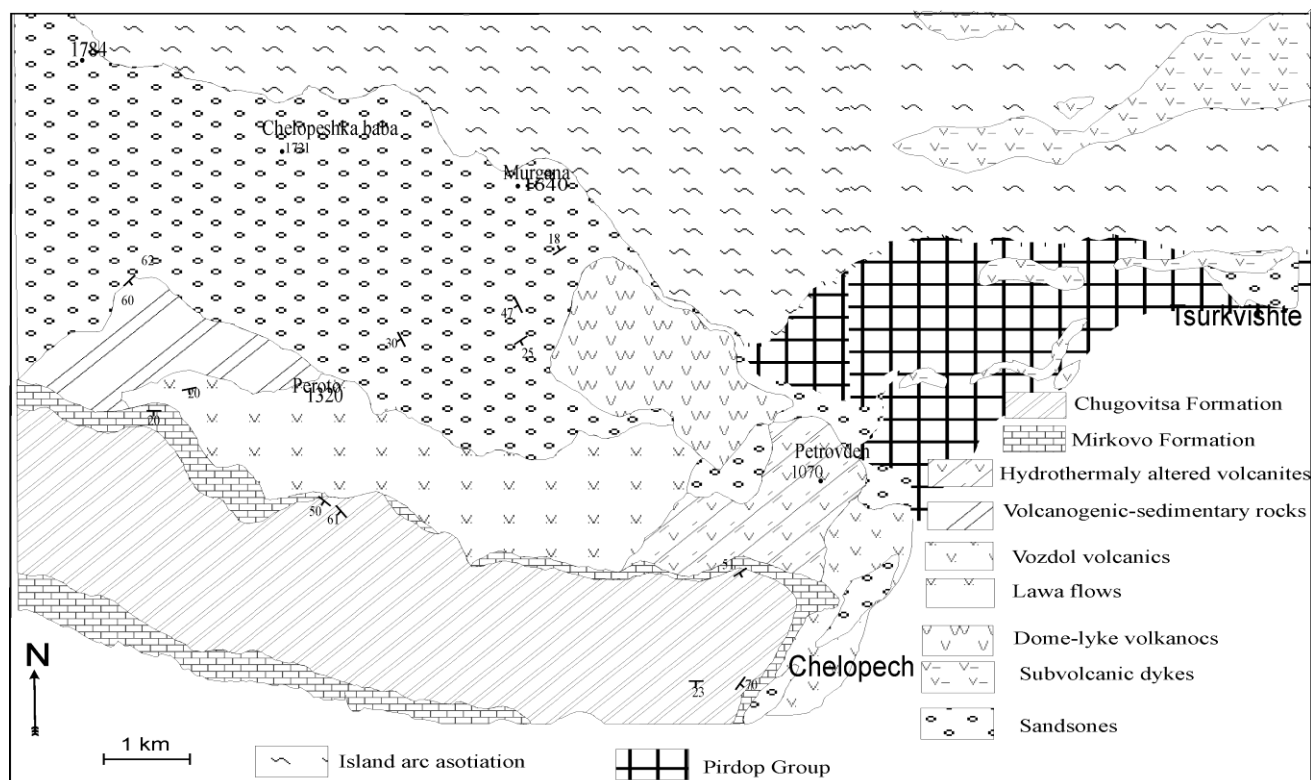


Fig. 1. Geological map of the Northern most part of the Panagyurishte region (after Stoykov et al., 2002) with addition

2004) divided the products of the Chelopech volcanic complex into 3 units: (I) dome-like volcanic bodies, (II) lava and agglomerate flows and (III) the Vozdol volcanic breccias and volcanites. The first unit is composed of dome-like volcanic bodies, which extruded through the unconsolidated Turonian sediments (the sandstone and coal-bearing formation) and through the metamorphic basement (Fig. 1). The largest volcanic body (Murgana) is approximately 2 x 1 km in size. It shows higher stage of phenocryst crystallization than other units. Brecciated fragments of the dome-like volcanic bodies have been observed as xenoliths in the third unit of the Chelopech volcanic complex – the Vozdol volcanic breccia. The dome-like bodies mainly have an andesitic and trachydacitic composition. They are highly porphyritic (phenocrysts >40 vol. %). The phenocrysts consist of plagioclase, zoned amphibole, minor biotite, titanite and rare corroded quartz crystals, whereas the microlites consist of plagioclase and amphibole only. The accessory minerals are apatite, zircon, and Ti-magnetite. The second unit is represented by lava flows, which grade upwards into agglomerate flows (with fragments up to approximately 30 cm in size). Borehole data shows that the total thickness of these volcanic products is generally less than 1200 m, but exceeds more than 2000 m in the region of the Chelopech mine ("within their extrusive center", Popov et al., 2002). The composition of the lava flows varies from latitic-trachydacitic to dacitic. Subsidiary andesites are also present. These volcanic rocks consist of the same phenocrysts, microlites and accessory minerals as the first unit, with the exception of the corroded quartz crystals. The lava flows contain fine-grained, fully crystallized enclaves of basaltic andesites to shoshonites. The enclaves consist of the same minerals as the main mass of unit 2 (plagioclase, amphibole and minor biotite), but comprise phenocrysts of different (more basic) chemistry. A fine-grained quartz zone marks the margins of the enclaves. These features

are typical for magma mingling and mixing processes and are mostly exhibited in the lava flows compared to the other volcanic units (Stoykov et al., 2002).

The third unit is represented by volcanic breccias and volcanites that formed the so called Vozdol monovolcano of Popov et al. (2000, 2002). The volcanic breccias contain fragments within their lava matrix that vary in size between 20 and 80 cm. Brecciated fragments from the andesites of the first unit can be observed in outcrops in the Vozdol river valley. The matrix of the volcanic body in the eastern part hosts small lenses and layers of sedimentary material (sandstones to gravelites), which abundance increases towards the margins of the body. The Vozdol volcanic breccias additionally intercalate and are covered by the Vozdol sandstones (Fig. 1), the latter palaeontologically dated as Turonian in age (Stoykov and Pavlishina, 2003). These features may suggest that the extrusion of the third unit volcanites occurred contemporaneous with sedimentation processes in the Turonian. In the breccias we can observe strongly hydrothermally altered volcanic xenoliths with an obliterated primary texture, so that we are not able to recognize, which type was the initial volcanic rock. Additionally there are missing detailed studies on the alteration type in these xenoliths; the latter are crucial, as it is not clarified, if the high sulfidation type alteration (leading to the deposition of the gold) was genetically linked with the widespread hydrothermal alteration along the Petrovden fault Fig. 1, Popov et al., 2000, Jeleu et al., 2003), hence it is not clear, if the observed xenoliths are related to the economic mineralisation, or not. The composition of the Vozdol volcanites varies from basaltic andesites and andesites to latites). They show similar petrographic characteristics to the older units although their phenocrysts (plagioclase, amphibole, minor biotite, and titanite) are less abundant. The groundmass is composed of microlites of the same nature as minerals of the second unit. K-feldspar is present as microlites only in the

Vozdol andesitic rocks. A biotite  $^{40}\text{Ar}/^{39}\text{Ar}$  age yields a Turonian age of  $89.95 \pm 0.90$  Ma (Velichkova et al., 2001; Handler et al., 2004).

The magma of the volcanic complex initially erupted more acid volcanic rocks. The earlier products (dome-like bodies and lava to agglomerate flows) contain 61–64 wt%  $\text{SiO}_2$  whereas the more basic Vozdol breccias and volcanites contained 55.5–58.0 wt%  $\text{SiO}_2$ .

The cover of the Chelopech volcanic complex is composed of the Vozdol sandstones (in the east), muddy limestones of the Mirkovo Formation (in the center) and sedimentary rocks of the sandstone and coal-bearing formation (in the west, Fig. 1).

## Regional tectonic evolution

The Alpine evolution of the Bulgarian tectonic zones is intimately linked to the tectonic evolution and closure of the Tethys (Dabovski et al., 1991). Boccaletti et al. (1974), Berza et al. (1998) and Neubauer (2002) suggest post-collisional detachment of the subducted slab as the trigger for the Late Cretaceous calc-alkaline magmatism and associated ore deposit formation in the Srednogorie zone. In contrast, based on the observation that subduction ceased in the early Cretaceous (Barremian), Popov (2002) has interpreted the Banat-Timok-Srednogorie zone as a rift. This appears to be in apparent conflict with the subduction-related scenario, but the arguments raised by Popov (2002) could be reconciled with the scenario of Boccaletti et al. (1974), Berza et al. (1998) and Neubauer (2002), if one considers the time lag between cessation of subduction and post-collisional slab break-off. More recently, based on regional lithogeochemical and radiometric age data from magmatic rocks, Kamenov et al. (2003) propose a roll-back scenario to explain the geodynamic setting of the Panagyurishte district. However, both slab detachment and roll-back scenarios are disputed by Lips (2002), who argues that conditions for such geodynamic settings were unfavourable in the Late Cretaceous due to the relatively low density and limited length of the young subducted slab, and he favours typical subduction-related calc-alkaline magmatism and associated ore formation processes. Despite the fragmentary tectonic data, the southern Panagyurishte ore district appears to be essentially characterised by strikeslip tectonics along the dextral Iskar-Yavoritsa shear zone (Ivanov et al., 2001) that is a geological setting with a pronounced differential regional stress.

## Analytical techniques

### Major and trace elements

Major and trace elements were analyzed by X-ray fluorescence (XRF) at the University of Lausanne, Switzerland. The rare earth elements (REE) were analyzed by ICP-atomic emission spectrometry following the procedure of Voldet (1993). A petrological study has also been performed. Mineral analyses on samples of the different units were carried out at the University of Lausanne on a CAMEBAX SX-50 electron microprobe.

## Petrography

The investigated dykes are classified as andesites, latites to dacites and trachydacites (Fig. 2). The  $\text{SiO}_2$  content of these rocks varies from 60.07 to 62.60 wt% (Table 1).

Table 1

Major element composition of the representative samples

Oxides wt. %	42Dy	49kD	105GD	108Ts	122GD
$\text{SiO}_2$	60.07	60.85	62.90	61.91	62.60
$\text{TiO}_2$	0.47	0.49	0.48	0.48	0.46
$\text{Al}_2\text{O}_3$	16.46	17.25	17.73	17.36	17.24
$\text{Fe}_2\text{O}_3$	4.04	4.53	4.40	4.45	4.24
$\text{MnO}$	0.20	0.21	0.14	0.14	0.15
$\text{MgO}$	1.61	2.02	1.48	1.26	1.22
$\text{CaO}$	5.34	4.34	3.30	3.09	4.35
$\text{Na}_2\text{O}$	3.69	4.25	5.41	3.78	4.07
$\text{K}_2\text{O}$	3.20	2.67	2.83	5.04	2.89
$\text{P}_2\text{O}_5$	0.20	0.17	0.20	0.22	0.19
LOI	3.71	3.00	1.12	2.21	2.82
Total	98.99	99.78	99.99	99.94	100.23

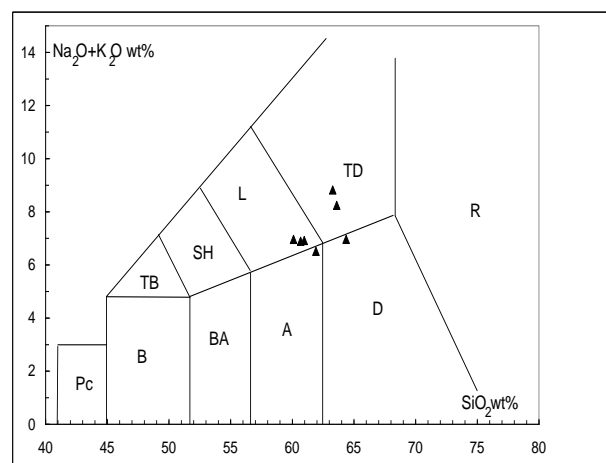


Fig. 2. TAS diagram after Le Maitre (1989) for representative dyke samples from the studied region (B—basalt; BA—basaltic andesite; A—andesite; D—dacite; SH—shoshonite; L—latite; TD—trachydacite)

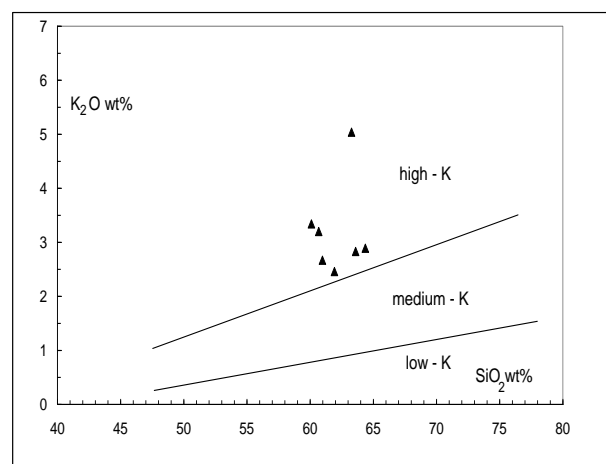


Fig. 3.  $\text{SiO}_2$  vs.  $\text{K}_2\text{O}$  diagram after Le Maitre (1989) for representative dyke samples

The phenocrysts (> 40 volume %) consist of plagioclase, zoned amphibole, minor biotite, and titanite; whereas the microlites consist of plagioclase and amphibole only. The accessory minerals are apatite, zircon, and Ti-magnetite. They contain rare fine-grained, fully crystallized inclusions consisting of the same minerals (plagioclase, amphibole and minor biotite) which comprise phenocrysts of different chemistry. The margins of the inclusions are marked by fine-grained quartz zone which is interpreted as evidence of magma mingling.

## Mineral chemistry

The composition of plagioclase phenocrysts (Table 2) of the investigated dykes varies from  $An_{39.2-47.7}$  (core) to  $An_{37.7-41.1}$  (rim). The rims are variable in composition and substantially overlap the field of the phenocryst cores (Fig. 2). The amphiboles (Fig. 4, Table 2) display Mg # between 0.48 and 0.57. The contents of Si p.f. u. range between 6.40 and 6.48 and they plot on the limit of the magnesiohastingsite, and hastingsite field of Leake et al. (1997).

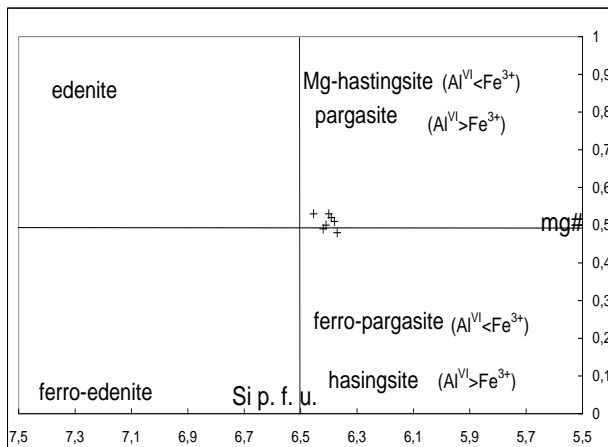


Fig.4. Classification of amphibole phenocrysts (after Leake et al., 1997)

Table 2

The plagioclase composition of the representative dyke samples

Sample	Pl/p4l	Pl/p5	Pl/p6	Pl/p3i	Pl/p4c
SiO <sub>2</sub>	58.30	58.82	58.59	58.16	58.06
TiO <sub>2</sub>	0.05	n. d.	n. d.	n. d.	0.21
Al <sub>2</sub> O <sub>3</sub>	25.78	25.77	26.00	26.53	27.17
FeO <sub>tot</sub>	0.27	n. d.	0.07	0.11	0.24
MnO	n. d.	n. d.	n. d.	0.21	0.12
CaO	8.49	8.54	8.65	8.08	8.86
Na <sub>2</sub> O	6.48	6.90	6.35	6.04	5.06
K <sub>2</sub> O	0.56	0.60	0.56	0.91	0.60
BaO	n. d.	n. d.	n. d.	n. d.	n. d.
Summe	99.93	100.63	100.22	100.04	100.32
Or	3.2	3.3	3.2	5.4	3.8
Ab	56.1	57.4	55.2	54.4	48.9
An	40.7	39.3	41.6	40.2	47.3

## Bulk rock trace elements composition

The MORB normalized patterns for the investigated dykes (Table 3, Fig. 5) indicate enrichment of LILE and in lesser degree of some HFSE (Ce, Zr, P and Hf) with a strong negative Nb anomaly and a depletion of the Fe-Mg elements. All these features are typical for subduction-related magmatic sequences due to the melting of sedimentary material of the subducted slab. In comparison to the volcanic rocks of an Andean-type active continental margin, the investigated magmatic rocks show small K<sub>2</sub>O, Ba and Hf enrichments and depletions of Nb, TiO<sub>2</sub>, Zr and P<sub>2</sub>O<sub>5</sub>.

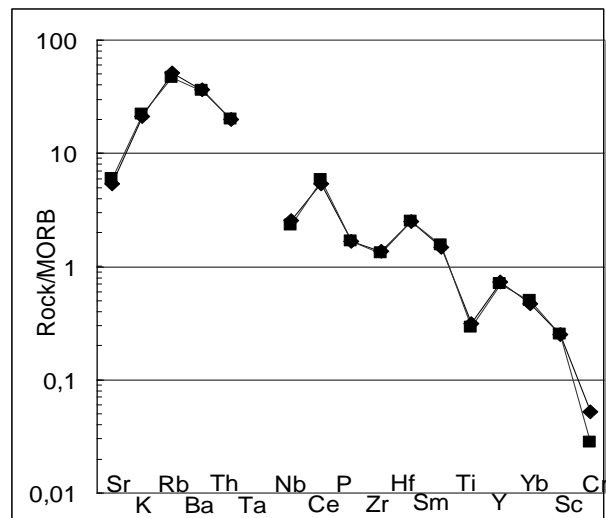


Fig. 5. Spider discrimination plot for the investigated dykes

These rocks have fractionated LREE and relatively flat HREE patterns (Fig. 6), as typically found in subduction related volcanic rocks. The LREE enrichment ranges from 33 to 80 times chondritic, whereas La<sub>n</sub>/Yb<sub>n</sub> ratios vary from 10 to 13. Middle and heavy REE show relatively flat patterns, generally within 5-30 times that of chondritic ones. An Eu anomaly is not observed, which suggests that there was no plagioclase fractionation involved in genesis of the studied andesitic rocks.

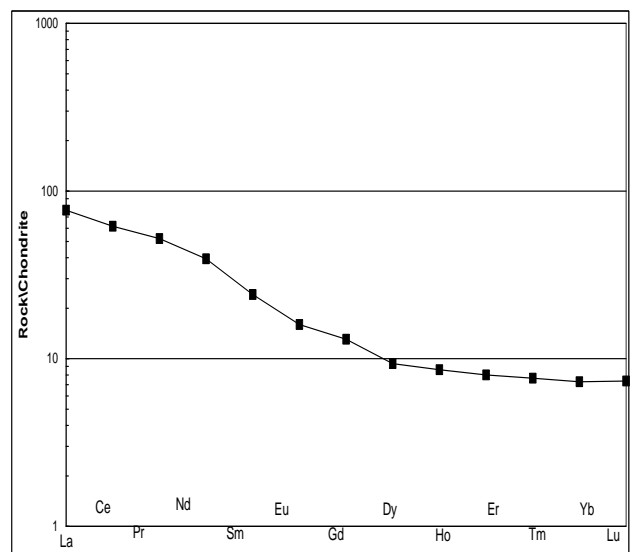


Fig. 6. Rock/chondrite diagram for the investigated dyke rocks

Table 3

Trace element composition of the representative volcanic samples

Elements (in ppm)	42Dy	49kD	105GD	108Ts	122GD
Nb	9	12	8	9	8
Zr	123	206	107	141	135
Y	22	27	22	26	22
Sr	641	794	1414	730	736
U	<2<	n.a.	<2<	4	3
Rb	102	86	87	113	99
Th	4	n.a.	3	7	7
Pb	13	n.a.	15	16	21
Ga	19	18	18	18	18
Zn	49	81	45	53	52
Cu	7	n.a.	4	8	5
Ni	2	n.a.	2	2	3
Co	7	n.a.	39	23	25
Cr	13	n.a.	9	8	9
V	89	90	92	84	79
Ce	51	n.a.	41	54	43
Nd	25	n.a.	20	32	22
Ba	726	780	612	793	771
La	39	n.a.	26	32	27
S	11	n.a.	<3<	<3<	<3<
Hf	6	n.a.	7	8	6
Sc	10	n.a.	7	5	7
As	7	n.a.	7	4	4
La	25.20	n.a.	28.30	n.a.	n.a.
Ce	53.30	n.a.	58.30	n.a.	n.a.
Pr	6.40	n.a.	6.00	n.a.	n.a.
Nd	24.80	n.a.	26.20	n.a.	n.a.
Sm	4.90	n.a.	5.10	n.a.	n.a.
Eu	1.23	n.a.	1.26	n.a.	n.a.
Gd	3.60	n.a.	3.30	n.a.	n.a.
Dy	3.20	n.a.	3.10	n.a.	n.a.
Ho	0.67	n.a.	0.69	n.a.	n.a.
Er	1.80	n.a.	1.80	n.a.	n.a.
Tm	0.26	n.a.	0.28	n.a.	n.a.
Yb	1.60	n.a.	1.70	n.a.	n.a.
Lu	0.25	n.a.	0.25	n.a.	n.a.

## Sr and Nd isotopes

### Rb-Sr and Sm-Nd whole rock isotope analyses

The isotopic composition of Sr and Nd and the determination of Rb, Sr, Sm and Nd contents were performed at the University of Geneva. The initial Sr ratios for the investigated dyke complex range between 0.7055 and 0.7060 (after 90 Ma correction). The Sr isotope ratios of the magmatic rocks from the Chelopech volcano display a small range between 0.7049 and 0.7054 after a 90 Ma correction (Stoykov et al., 2002).

Generally  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios fall within the field previously defined by Kouzmanov et al. (2001) values from 0.7046 to 0.7061 (after 80 Ma correction) for the volcanic (andesites and

dacites) and plutonic (granodiorites and granites) rocks from the southern part of the Central Srednogie volcano-intrusive area. The Nd isotope ratio for the investigated dykes varies from 0.512449 to 0.512450 (after 90 Ma correction). The calculated  $\epsilon_{90}(\text{Nd})$  values are between -2.27 and -3.55. These data are similar to Sr and Nd isotope composition of the Chelopech volcanites and the Elatsite subvolcanic rocks (Stoykov et al., 2004). They suggest a mixed mantle-crust source of the Turonian magmatism in the Chelopech region. However using the variations of the initial Sr and Nd ratios vs.  $\text{SiO}_2$  the evolution of the magma may be largely due to mingling/mixing processes, without isotope homogenisation in the whole volume of the magma chamber, and not to a simple differentiation of one parental magma, combined or not with assimilation of upper crustal rocks (Stoykov et al., 2004).

## Conclusions

The investigated dykes are classified as andesites, latites to dacites and trachydacites. Their phenocrysts (> 40 volume %) consist of plagioclase, zoned amphibole, minor biotite, and titanite; whereas the microlites consist of plagioclase and amphibole only.

The MORB normalized patterns for the investigated dykes indicate enrichment of LILE and in lesser degree of some HFSE (Ce, Zr, P and Hf) with a strong negative Nb anomaly and a depletion of the Fe-Mg elements. All these features are typical for active continental margin. These rocks have fractionated LREE and relatively flat HREE patterns, as typically found in subduction related volcanic rocks. The LREE enrichment ranges from 33 to 80 times chondritic, whereas  $\text{La}_n/\text{Yb}_n$  ratios vary from 10 to 13. Middle and heavy REE show relatively flat patterns, generally within 5-30 times that of chondritic ones. An Eu anomaly is not observed, which suggests that there was no plagioclase fractionation involved in genesis of the studied andesitic rocks.

The initial Sr ratios for the investigated dyke complex range between 0.70550 and 0.70601 (after 90 Ma correction) and the Nd isotope ratio varies from 0.512449 to 0.512450.

The combined petrologic, isotope-geochemical and geochronological investigations of the dyke complex in the Zlatitsa pass suggest similar composition compared to the Chelopech volcanites and the Elatsite subvolcanic rocks

The petrological and geochemical features give additional evidence for a possible uniform magma chamber of the volcanic rocks in the Chelopech and Elatsite deposits (Stoykov et al., 2004) and the investigated dyke complex in the Zlatitsa pass with a complex evolution in Turonian times, when a combination of processes of magmatic differentiation, assimilation, mingling and mixing took place. These magmatic products reveal similar Sr and Nd characteristics (Stoykov et al., 2002, von Quadt et al., 2002), where the tendency of an increase of initial Sr and Nd isotope ratios related to minor assimilation of host rocks within parts of the magmatic chamber. The amphibole chemistry of the magmatic units of both deposits and the investigated dyke complex shows some similar characteristics – Mg# between 0.48 and 0.67 and Si per formula unit content between 6.40 and 6.55, but mark

differences comparing to the other deposits of the Panagyurishte ore region (Stoykov et al., 2002, Kamenov et al., 2003).

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