

## SHIVACHEVSKI COMPLEX METAGRANITES - GEOCHEMICAL CONSTRAINTS

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### Introduction

Formation and deformation evolution of the pre-Mesozoic basement of the Balkanides in Stara Planina mountain is a major topic of controversy for the understanding of the tectono-metamorphic evolution of the Balkanides since the Paleozoic (Ivanov et al., 1987; Haydoutov, 1991). It is believed to consist of non-metamorphosed sediments and metamorphosed in greenschist facies (locally reaching migmatization) volcanic-sedimentary sequence. The metamorphosed sequence is considered to have heterogeneous origin of large continental and oceanic crust fragments included in clastic to carbonate sediments. Late Palaeozoic calc-alkaline granitoids and K-alkaline plutons intrude the metamorphosed and the non-metamorphosed sequence forming contact aureoles. However, our understanding remains very limited due to restricted amount of geochemical and isotopic data.

Here we discuss the origin of Shivachevski metamorphic complex, part of the pre-Mesozoic basement in Tvardishka Stara Planina mountain. It is introduced by Ivanov et al. (1974) as volcanic-sedimentary sequence, subjected to regional-contact K-metasomatism by small leucogranite bodies intrusion, then regionally metamorphosed in greenschist facies. Later Haydoutov (1991) associated this metamorphic complex to the island-arc Berkovska Group of the Balkan-Carpathian Ophiolite Segment as metatectites, formed over intermediate to acid volcanic rocks.

### Petrography

Recent structural end petrographic data showed that metagranites are the major lithotype in Berkovska Group from Central Balkan area, including the discussed Shivachevski complex (Statelova & Machev, 2004). Statelova & Machev (2004) argued that metamorphites are porphyritic (K-feldspar) granites with gneissic structure, which are non-uniformly deformed from ductile to brittle. On a micro-scale preserved primary igneous textures are observed in less deformed parts of the complex. The primary texture shows euhedral inclusions of plagioclase, quartz and biotite in K-feldspar growth zones, zoned plagioclase, K-feldspar Carlsbad twinning, primary igneous epidote inclusions in biotite, etc. The mineralogical association of the metagranites is K-feldspar, plagioclase, quartz, biotite ± amphibole. Based on deformation and mineralogical association, Statelova & Machev (2004) concluded that the metamorphic conditions did not exceed 400°C because white mica replaces large amount of plagioclase, whereas chlorite replaces biotite and epidote mostly the plagioclase cores. Below 400°C, feldspars can be fully chemically re-equilibrated whereas biotite will remain passive. However, moderate to low temperature recrystallisation > 300°C of biotite is possible (Voll, 1976; Simpson, 1985) as small biotite flakes are found along shear bands.

The geochemical data presented in this study includes rock samples of less to strongly deformed porphyritic medium to large grain size metagranites from all parts of Shivachevski complex. Also presented are data of amphibole rich orthometamorphites. These are found as rare dm-scale elongated lenses with penetrating foliation and sharp contacts in all levels of the complex. General assumption of isochemical metamorphism in the scale of the complex is made based on the relative quantities of the alteration minerals and the altered minerals. The effect of fluidally induced element exchange between levels with different deformation ratios is reduced by sampling most of these levels.

### Major and trace elements

The metagranites of Shivachevski complex are peraluminous to metaluminous (Fig. 1a), corresponding to appearance of normative corundum of 0-2,8 wt%. The investigated rocks plot in the (monzo)granodioritic to granitic (SiO<sub>2</sub> 62,8-72,2 wt%) fields of the classification diagrams based on whole rock chemistry or normative mineral compositions for granitoids. This corresponds to the high presence of normative plagioclase (35,9-53,6 wt%) against normative K-feldspar (16,6-26,8 wt%). According to the nomenclature of igneous series based on K<sub>2</sub>O vs SiO<sub>2</sub>, they belong to the high-K calc-alkaline series (Fig. 1b). However, given the K<sub>2</sub>O/Na<sub>2</sub>O ratio between 0,7 and 1,2, the subalkaline character of the metagranites is controlled by both K and Na.

No compositional variation is associated with the spatial position of the samples (Fig. 1, Southern parts represent the upper level of the complex according to its present position). The typical igneous trends (Fig. 1b and 2) of the compositions are the same plotted vs SiO<sub>2</sub> or vs TiO<sub>2</sub> or vs DI (Thornton-Tuttle Differentiation index).

More intermediate compositions represent the amphibole rich elongated lenses, found in all levels of the complex. They have smaller differentiation index (82,86–87,83 %) and higher magnesium ratio (MgO/MgO+FeO<sub>tot</sub> 41,46-47,76%), corresponding to the igneous trends observed. The slight increase of aluminium saturation index versus more acid compositions in Fig. 1a is also observed in the Al<sub>2</sub>O<sub>3</sub> harker plot (Fig. 2.). This could be due to amphibole separation during igneous crystallization (Zen, 1986), based also on the observed mineral assemblages in the lenses.

The investigated metagranites show some characteristics of I-type granites, e.g. A/CNK(mol) < 1,1 and large variation in SiO<sub>2</sub> contents (59-73 wt%). Their high K<sub>2</sub>O content (average 3,86 wt%) in conjunction with high Ba content (1041-2026 ppm) are unusual characteristics for such granite. This would suggest that a potassium-bearing phase has contributed significantly during their formation via partial melting. In addition, the high CaO (0,9-5 wt%) and MgO (0,5-2,9) contents

would suggest the occurrence of mineral enriched in Ca and Mg. The Ta/Nb ratio (0,02-0,04) shows depletion in Ta and enrichment of Nb suggesting that the mineral is amphibole.

Furthermore, the values of K/Rb (246–322), K/Ba (16–

31), and Ba/Rb (8–18) do not vary with the DI index, arguing against feldspar segregation during melting. However, the large variation in these ratios reflects possibly the migration of LIL elements during metamorphism and deformation.

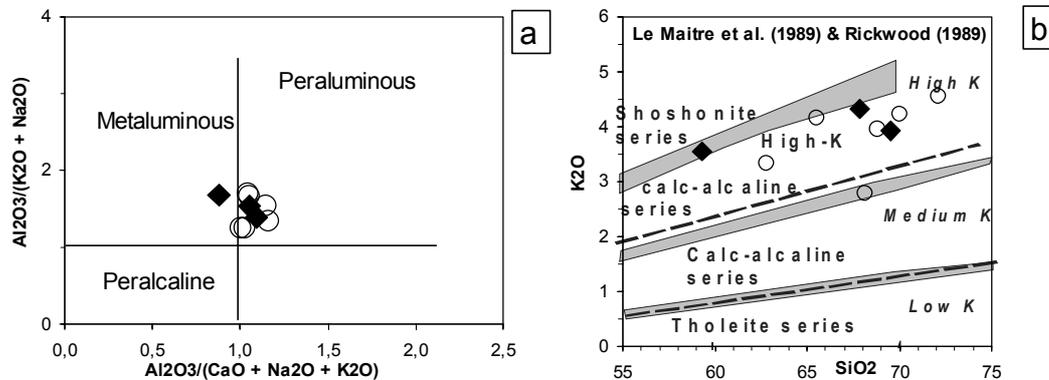


Fig. 1. Aluminium saturation (a) and series (b) plot of Shivachevski complex. Aluminium saturation index as molar ratio. Plot b: nomenclature in italic and dashed lines after Le Maitre et al. (1989); nomenclature in normal font and boundary fields summarised by Rickwood (1989), based on Peccerillo and Taylor (1976), Ewart (1982), Innocenty et al. (1982) and others. Black rombs - samples from the Southern parts of the complex; open circles - samples from the Northern parts of the complex.

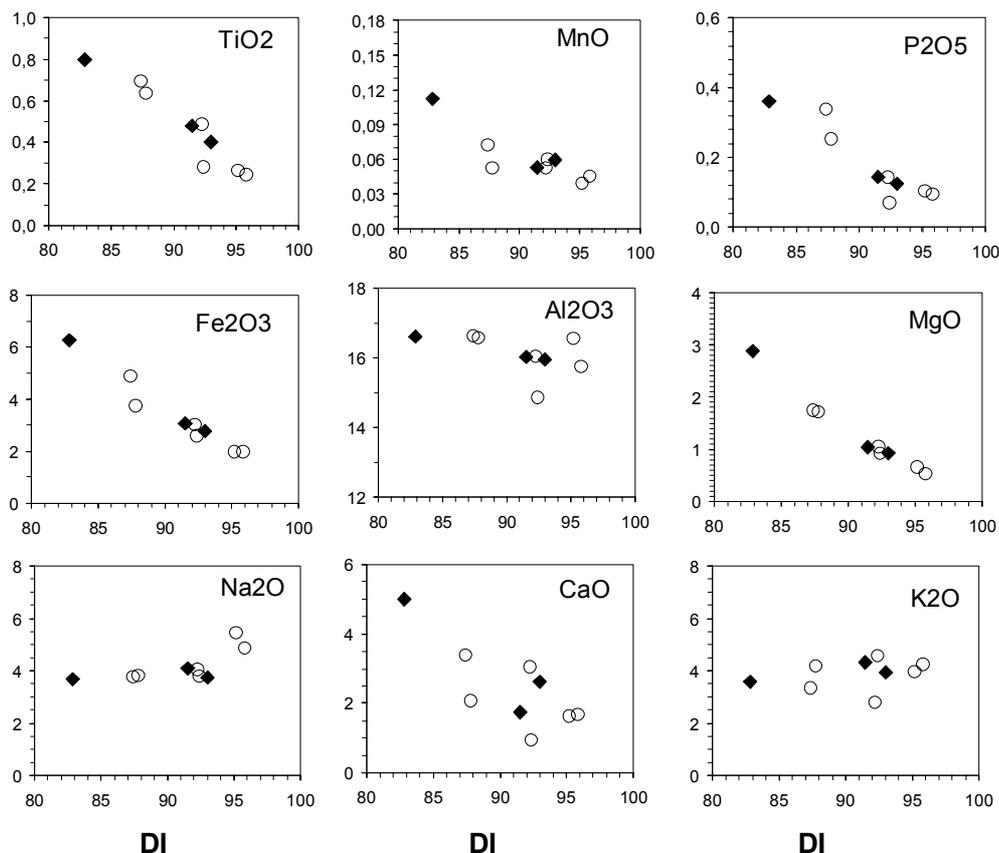


Fig. 2. Harker plots of major oxides (wt%) against Differentiation Index (Thornton-Tuttle) for Shivachevski complex. Black rombs - samples from the Southern parts of the complex; open circles - samples from the Northern parts of the complex.

The chondrite-normalized REE patterns of all data are presented in Fig. 3. The LREE fractionation against HREE is not very strong, but in very large variation limits ( $La_N/Yb_N$  9-42). The slight negative Eu anomaly is clearly related to the Si contents and the DI index. More basic compositions show larger Eu anomaly (Fig. 3), probably reflecting light plagioclase fractional crystallization.

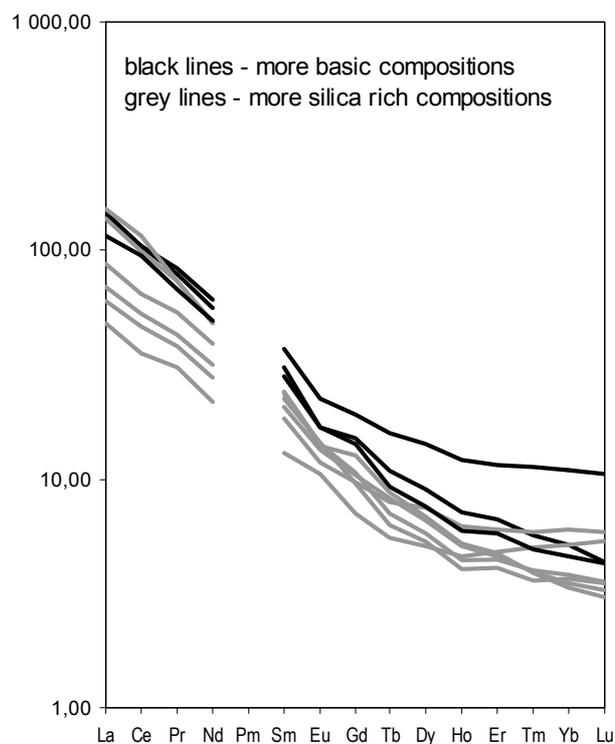


Fig. 3. Chondrite-normalised REE patterns of samples from Shivachevski complex. Normalising values after Boynton et al (1980)

The lack of distinctive negative Eu anomaly combined with the low fractionation of LRE/HRE elements, the plagioclase/K-feldspar ratio, and the high Ba, K, Ca contents could be due to: (1) higher degree of melting to produce rhyolitic magma in equilibrium with the feldspar source, combined with weak fractional crystallization of plagioclase; (2) regardless of the

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degree of melting, the melt produced to be of dacitic to andesitic composition, where Eu becomes incompatible in plagioclase (Schnetzler & Philpotts, 1970; Gill, 1981; Bacon & Druitt, 1988 and others) again with weak fractionation of plagioclase during crystallization. Both cases imply different melting settings and should be supported by further isotopic investigations and REE modeling of the melting-crystallization processes.

## Discussion and conclusion

The preserved structures and textures of the investigated rocks and their geochemical characteristics provide crucial information on their origin and on their formation. Based on data provided here we argue that the processes of K-metasomatism or migmatization of a volcanic-sediment sequence, reported by previous authors have led to the formation of Shivachevski complex. The petrographic evidence of granites as protoliths of Shivachevski complex, metamorphosed in greenschist facies during intense non-uniform deformation, is supported by geochemical analyses, showing clear igneous trends and characteristics. The granites followed nicely the differentiation trend with little or no fractionation of feldspars during crystallization. The elongated amphibole-bearing lenses with sharp contacts could represent earlier fractionations of the same magma, however more data should support such a model.

The geochemical characteristics of the intermediate to felsic volcanites of Berkovska group, summarized in Haydoutov (1991) show large variations in compositions, thus comparison between these and the metagranites of Shivachevski complex in silica or aluminium saturation is irrelevant, as well as in most of the major elements. However, published data show higher  $Na_2O/K_2O$  ratio, controlled by lower  $K_2O$  content, in addition to lower Rb, Sr and Ba contents. This could be due to difference in igneous origin and evolution, or to LIL elements loss during metamorphism, which is relatively higher in the outcrops as reported by Haydoutov (1991).

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