MINERALOGY AND CHEMISTRY OF BIOTITES FROM THE BELOGRADCHIK PLUTON - SOME PETROLOGICAL IMPLICATIONS FOR GRANITOID MAGMATISM IN NORTH-WEST BULGARIA

Philip Machev[1], Laslo Klain[2], Lutz Hecht[3]

[1,2] St. Kliment Ohridski University, Faculty of Geology & Geography, 1504 Sofia, Bulgaria.
[1] machev@gea.uni-sofia.bg
[3] Museum fьr Naturkunde, 43 Invalidenstrasse, 10115 Berlin

Biotite is a common hydrated ferromagnesian silicate in most mafic, intermediate and felsic plutonic rocks. Igneous biotite covers a wide range of crystallization conditions and reacts very sensitively to changes in the physico-chemical conditions such as oxygen and halogen fugacities, temperature, pressure and chemical composition of the magmas (Speer, 1984). In addition, the classical experimental work of Wones & Eugster (1965) clearly established this mineral as a valuable indicator of redox conditions in granitic magmas. Biotite also reflects the nature and tectonic environments of their host magmas (Abdel-Rahman, 1994).

Trioctahedral true micas of the annite-phlogopite, eastonite-siderophyllite solid solutions (*i.e.* biotite) can by virtue of their crystal structure accommodate most of the common elements present in granitic magmas. The following features make biotite a valuable probe of magma composition: 1) It is the most important reservoir of any excess aluminium in granites that do not have important amounts of garnet, cordierite or Al_2SiO_5 polymorphs; therefore it directly reflects the peraluminosity of the host magma in such rocks, and 2) it is the most readily available indicator of oxidation state. Magma peraluminosity and relative oxidation state have been the basis for subdivision of granites into S- and I-types (Chappell & White, 1974) and into ilmenite and magnetite series (Ishihara, 1977) respectively.

In this study we document by electron microprobe the chemical composition of biotites from the Belogradchik pluton (NW Bulgaria) aiming at determination of their occurrence, structural formulae, crystal chemistry and crystallization conditions. Secondly, we attempt to obtain the controlling and catalytic effect of biotites for crystallization of secondary potassium feldspar and Ca-Al silicates and discriminate the tectonic settings of the pluton using the biotite composition.

The Belogradchik pluton (Dimitrova, 1965) forms a strongly elongated body in NW-SE direction. It consists of mainly equigranular biotite-bearing granites with rare K-feldspar megacrysts and is a part of the Stara planina Ca-alkaline formation (Dimitrov, 1932, 1939). The primary intrusive contacts were tectonically reactivated and sedimentary rocks of Paleozoic age overthrusted the pluton. On the other hand, it was thrusted over Triassic, Jurassic and Cretaceous sediments (Tchounev et al., 1964; Haydoutov, 1995). The uranogenic model ages gives data about 265-270 Ma for the Belogradchik pluton (Amov, Arnaudov, 1981). The granites of Belogradchik pluton are high-potassium, calc-alkaline, strongly metaluminous with normative diopside (I type). The major rock-forming minerals are zoned plagioclase ($An_{22.6-37.6}$), potassium feldspar (microcline), biotite, quartz. Ilmenite, apatite, zircon, alanite are the main accessory phases. Secondary muscovite and chlorite replaced biotite and plagioclase. The granites underwent a high temperature subsolidus deformation which caused the formation of primary foliation parallel to the main direction of pluton elongation. This circumstance, together with S-like curved chlorite lenses in pegmatite veins indicate an intrusion in dextral transtensional regime.

The biotite occurs as euchedral to subhedral flakes that vary from 0.5 to 2 mm in diameter. In the deformed parts it defines a planar fabric and is concentrated in narrow bands. Biotite is dark brown to yellow. Biotite exhibits a remarkable increase in total Al (1.59-1.69 pfu) and considerable iron enrichment [$Fe_t/(_{Fet}+Mg)$] in the range 0.6-0.64 with composition near the annite-siderophyllite line. The relatively low $Ti0_2$ content (2.97-3.5 %; 0.17-0.21 Ti pfu) and high Al^{VI} (0.27-0.36 pfu) reflect the conditions of crystallization (abyssal level). The peraluminosity index (A/CNK) of biotite (1.69-2.03) is considerably higher relative to that of the host rock and confirms biotite as the most common mineralogical sink for excess aluminium in granitic rocks in general.

The Fe^{3+}, Ti^{4+} and Al^{VI} contents in the biotite are the most important elements to be considered for understanding of petrogenetic problems in granitic rocks (Taylor, 1964; Buddington & Lindsley, 1964). The contents of Ti^{4+} and Fe^{3+} depend mostly on temperature of crystallization and oxygen fugacity (fO_2), while Al^{VI} is a variable that depends especially on the Al activity. The Fe^{3+} content and $Fe_t/(Fe_t+Mg)$ ratio provide at least relative information about the oxygen fugacity during crystallization (Wones & Eugster, 1965; Neiva, 1981). Because we have only microprobe analyses of biotites from the Belogradchik pluton (all estimated iron is as FeO) to determinate the oxygen fugacity ($\log fO_2$), the diagram of Wones & Eugster (1965) modified by Shabani & Lalonde (2003) was used. Compositions of investigated biotites fall mainly on the NNO buffer ($\log fO_2 = 10^{-14,3}$ - $10^{-15,8}$ bars) reflecting relatively lower oxidizing conditions. This fact is in good agreement with the presence of ilmenite as the main oxide phase in the rocks.

A special feature of biotites from the Belogradchik pluton are the lenses of potassium feldspar (Kfs) and prehnite developed along fracture planes in the crystals (Fig. 1, 2). In particular, Kfs is observed only in fresh biotite flakes, while prehnite occurs in partly choritized biotite, too.

In both cases the cleavage planes of the host mineral are curved, the borders are sharp and undulatory extinction in the biotite around the pod like prehnite is not pronounced. Prehnite is colorless, indicating a birefringence of about 0.03 and has the following summarized formula:

$$Ca_{3.56\text{-}3.81}Fe^{3+}_{0.2\text{-}0.34}Al^{VI}_{1.73\text{-}1.97}(Si_{5.99\text{-}6.16}Al_{1.84\text{-}2.01})_{20}(OH)_4$$

The Kfs in the biotite differs by composition from the Kfs in the rocks. It has higher FeO content (0.48-0.67 wt %) and is richer in Or component ($Or_{97.5\text{-}98.5}$)

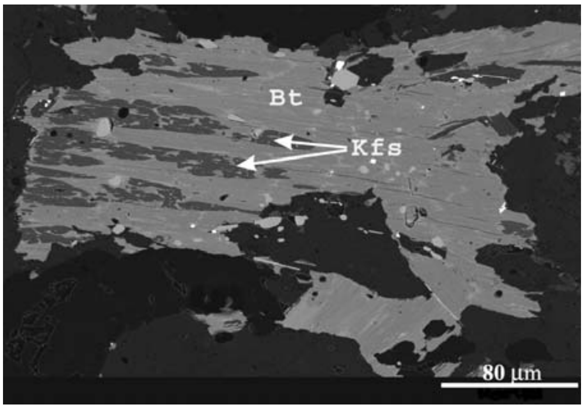

Fig.1. BSE-image of potassium feldspar fingering into the biotite cleavage.

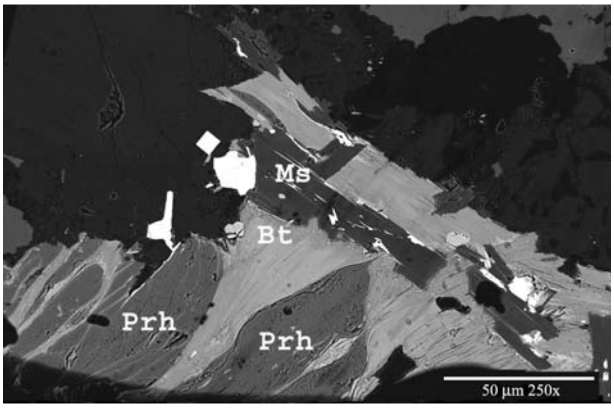

Fig.2. BSE-image of thin lenses of prehnite developed along the biotite cleavage.

The origin of secondary Ca-Al silicates as lenses that grow parallel to the cleavage of biotite is a disputable problem with two main tendencies. It may be a result from later, post-magmatic process, like chloritization and sericitization caused by meteoric fluids or may be caused by late-magmatic (deuteric) fluids connected with the parental magma and probably saturated in many elements (Ca, K u.a) during post-magmatic cooling. The lense-like shape and the preferential growth within biotite might be caused by: 1) a local suitable chemical environment within the biotite, or 2) a catalytic effect (Boles & Johnson, 1983; Nijland et al., 1994). The first reason might be true if the biotite represented a local chemical trap for crystallization of Ca-Al cilicates; however Ca is absent in the host biotite. Furthermore, the Ca-Al silicate grains in biotite do not indicate biotite replacement but rather enlargement and bending of the biotite cleavage and thus biotite remains stable. The second reason assumed that lattice defects within the biotite structure (e.g. Al^{3+}«Si^{4+}), which caused incipient leaching of K^+ ions from the cleavage surface, lead to an attraction of H^+ onto the negative charged biotite cleavage surface. This produces a local decrease in H^+ concentration in the pore water (increase in pH) and induces crystallization of Ca-Al silicates or other minerals like carbonate or potassium feldspar (Boles & Johnson, 1983). In our study we consider that this catalytic effect at the biotite cleavage is the main reason for the preferential crystallization of prehnite and Kfs within biotite.

The formation of Ca-Al silicates within Ca-free biotite requires that Ca was intruded by a fluid phase. Late-magmatic (deuteric) fluids, probably saturated in many elements including K and Ca, would become oversaturated during the cooling of the pluton. Tulloch (1979) proposed the hydrothermal alteration of plagioclase as a probable source for Ca but in our case intense alteration of plagioclase to sericite was not observed. The composition of prehnite depends on temperature, pressure and fO_2. The upper P-T stability for prehnite in metabasites may reach 400 °C (Frey, et al., 1991) and up to 3 kbar. According to Freiberger et al. (2001), the cooling of a granitoid pluton begins at solidus conditions at about 650-700 °C. The first Ca-Al silicate that forms at a temperature 350-400 °C is hydrogarnet. We have not observed hydrogarnet lenses in biotite from the Belogradchik pluton but this mineral is widespread in the neighboring Sveti Nikola pluton. We assume that under the P-T conditions of hydrogarnet formation Kfs crystallized, instead. After that the fluids became oversaturated in Ca, and with temperature decreasing during cooling of the pluton, the prehnite was a stable phase and formed pod-like lenses along the biotite cleavage planes.

The application of biotite chemical composition to determine the nature and tectonic environments of their host magmas (Abdel-Rahman, 1994) does not give explicit conclusions in this study case. The data plot mainly in the fields of biotites from peraluminous granites. This circumstance is in contradiction with the geochemical characteristics of the Belogradchik pluton (metaluminous with normative diopside). The high Al_2O_3 content in the biotites probably was related with the fact that biotite is the most important reservoir of any excess aluminium in granites. This circumstance poses the problem correct usage of any discrimination diagrams.

In the present study, on the basis of textural and paragenetic evidence as well as mineral stability data, it has been shown that the potassium feldspar and prehnite formed as very early post-magmatic phases during the cooling of the pluton, predating all other pervasive hydrothermal alterations that occurred under lower pressure. The source fluids were deuteric, extracted from the source magma. The widespread presence of late-magmatic Kfs and prehnite in the Belogradchik pluton, and of hydrogarnet in Sveti Nikola pluton, is a special mineralogical feature of the Hercynian granitoids of North-West Bulgaria. It reflects the P-T conditions of crystallization and late magmatic evolution of the fluid phase.

The Belogradchik pluton was formed in postcollisional setting (the second tectonic model for the origin of high –K, I-type rocks after Roberts & Clements, 1993) by decompression following crustal thickening. The dominant tectonic regime was dextral transtensional in the sense of Dewey et al. (1998).

Acknowledgments

The investigations were financially supported by the Fund for Scientific researches of the “St. Kliment Ohridski” University (Grant 3553/2004) and the cooperation between Faculty of Geology & Geography and Museum fьr Naturkunde, Humbold University, Berlin.

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