



New data on the magmatism and the magmatic fluids of the Kožuf volcanic massif, Macedonia

Нови данни за магматизма и магматичните флуиди на вулканския масив Кожуф, Македония

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Geology

The Kožuf volcanic massif is disposed in the frame of the Vardar zone. The Pliocene volcanic and volcano-sedimentary rocks overlay the metamorphic (Precambrian and Paleozoic) and sedimentary (Triassic to Upper Eocene) rocks of the region (Janković et al., 1997; Boev, Jelenković, 2012). They occur as layers in a lacustrine basin and subvolcanic bodies crosscutting Triassic carbonates (Percial, Radke, 1994). The Pliocene volcanism is strongly explosive and predominating rocks are volcanoclastic (pyroclastic tuffs and breccias), accompanied by epiclastic conglomerates. The K-Ar age determinations of the volcanic rocks are between 6.5 and 1.8 Ma (Janković et al., 1997 and references there in). They are represented by shoshonites, latites, quartz latites, dacites, trachytes, and rhyolites. Latites and trachytes are the most widespread rocks. Subvolcanic rocks are represented by latites and dacites (Percial, Radke, 1994), trachytes (Boev, Jelenković, 2012) and monzonite porphyrites. These rocks represent small isometric outcrops supposed to be remnants of the conducting channels for the volcanism. The monzonite porphyrites outcrop SE of the Alshar deposit with diameter of the body about 50–70 m. The Alshar Au-As-Sb-Tl-Hg deposit is mainly hosted in Triassic carbonate rocks but the hydrothermal fluids have altered and ore contaminated the subvolcanic and volcanoclastic rocks.

Petrography and geochemistry

All volcanic and subvolcanic rocks are porphyritic with phenocrysts of plagioclase, clinopyroxene, amphibole, biotites, sanidine. In volcanic rocks amphiboles and biotites are often opacitized and amphiboles are altered in most of the cases. The mineral composition is based on 88 microprobe analyses (41 of this study). Pyroxene

decreases toward the more acidic rocks (absent in rhyolites) and is represented by diopside to augites (Mg# 0.9–0.76). Sanidine ($\text{Or}_{57.5-38}\text{Ab}_{36-59}\text{An}_{6.6-3.8}$) is lacking in shoshonites and increases in quantity toward trachytes. Biotites are often red-brown (Mg# 0.6–0.56). The groundmass in most of the cases is recrystallized, but hyalopilitic and trachytic texture are also found. Accessory minerals are apatite, titanomagnetite, rare ilmenite and rounded zircons. The established monzonite porphyrites has phenocrysts of plagioclase ($\text{An}_{36.6-42.3}\text{Or}_{2.5-8}$), clinopyroxene (Mg# 0.68–0.67) and biotite (Mg# 0.68–0.71, plotting at the biotite–phlogopite border line). The groundmass is holocrystalline, hypidiomorphic, composed of euhedral plagioclases, anhedral alkali feldspars ($\text{Or}_{57.5}\text{Ab}_{36-38}\text{An}_{6.4}$) and rare isometric clinopyroxenes.

The geochemical characteristic of the Pliocene magmatic rocks from the Kožuf massif is based on 52 whole rock analyses (Janković et al., 1997; Yanev et al., 2008; Boev, Jelenković, 2012 and 5 of this study). We do not dispose with samples from dacites and rhyolites and their characterization is based on the data from the already enumerated publications. Trace elements characteristics for the studied rocks are from 20 (5 of this study) analyses from the same publications. The major part of the analyses from Kožuf plot in the Si saturated fields and belong to the high-K series. Only dacites belong to the calc-alkaline rocks (low-K series). On major element Harker diagrams are established general trends of K_2O , CaO, MgO, FeO, TiO_2 , P_2O_5 decreasing with silica increasing. For trace element Harker diagrams the trends are not so well pronounced. In general Cr, Ni, Cu, Nb, Y decrease and Rb, Sr, U, Th, Tl, Ba increase with Si augmentation.

The chondrite normalized REE patterns show enrichment of LREE relative to HREE and in most of the cases relatively well pronounced negative Eu anomaly. All the Primordial Mantle normalized spidergrams

show negative anomalies for Ta, Nb, and Ti characteristic for synsubductional magmatism (Boev, Yanev, 2001; Yanev et al., 2008).

The rock diversity could be partly ascribed to the fractionation of clinopyroxene, amphibole, biotite, magnetite, plagioclase and apatite. Some peculiarity of the zonal arrangement of the plagioclase let us suppose the possible influence of magmatic mixing to the magmatic rock diversity. The role of the contamination is suggested by Yanev et al. (2008). The pressure of amphibole crystallization (after the geobarometer of Johnson and Rutherford, 1989) is about 7 kbars. The estimated temperature of apatite saturation and the apatite-biotite equilibrium (Harrison, Watson, 1984; Sallet, 2000) are about 950 °C; fO_2 is estimated to 2.8 units above the QFM buffer (Spenser, Lindsley, 1981).

Fluids in magma

The presence of fluid containing minerals even in the most basic volcanic rocks is an indication of the high fluid concentration in the magma. In latites and dacites the water content is determined to be about 6–7 wt.% (after the geohydrometer of Merzbaher and Eggler, 1984). In clinopyroxenes of the subvolcanic monzonite porphyrites are established magmatic rounded sulfide inclusions (pyrrhotite and bornite) with dimensions 10–30 μm . The composition of pyrrhotite gave us the opportunity to have an estimation of the fugacity of S (after Toulmin, Barton, 1964; $\lg fS_2 = 1.4$). Based on the chemical composition of apatite the estimated preeruptive content of Cl is 0.02–0.7 wt.% and the F content is about 0.15–0.39 wt.% (after Matez, Webster, 2005).

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